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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXIII. CONDENSATION OF THE ISOMERIC 2,3-BUTANEDIOLS WITH ETHYL ACETOACETATE[1]

BY A. C. NEISH[2]

Abstract

levo-2,3-Butanediol will condense with ethyl acetoacetate in the presence of hydrochloric acid to give the ethyl ester of *levo*-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane (I) (yield 48%) from which the free acid may be obtained. If *p*-toluenesulphonic acid is used as the catalyst and the condensation is carried out in boiling butanol with continuous removal of water, the butyl ester of (I) is obtained (yield 87%). Compounds described for the first time are *levo*-, *dl*-, and *meso*-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentanes, their *n*-butyl and *p*-bromophenacyl esters (melting points 74.5°, 76°, and 76° C., respectively) and the ethyl ester of the *levo*-isomer.

Previous work has shown that one of the most striking chemical properties of 2,3-butanediol is the ease with which it forms cyclic acetals and ketals (1, 4); this is particularly true of the *levo*-isomer. This paper describes the cyclic ketals of 2,3-butanediol obtained through reactions involving esters of acetoacetic acid, and thus serves to extend our knowledge of the chemistry of 2,3-butanediol.

Acetoacetic acid is too unstable to condense directly with 2,3-butanediol but the commercially available ethyl ester will react readily at room temperature, in the presence of hydrochloric acid, to give the ethyl ester of 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane. The yield obtained (*levo*-isomer) was only 48% of the theory, partly because the reaction is reversible but also because of side reactions such as hydrolysis and decarboxylation. If the reaction is conducted in boiling benzene using *p*-toluenesulphonic acid as a catalyst and removing the water as it forms the yield is slightly poorer, probably because of loss of the ethyl ester groups due to hydrolysis or alcoholysis. A good yield of the butyl ester of this ketal can be obtained, however, by carrying out the condensation in an excess of boiling *n*-butanol. The butanol is allowed to distil slowly from the reacting mixture in order to remove the water. In this way yields up to 87% of the theory were obtained. The isomeric *levo*-, *dl*-, and *meso*-butyl esters of 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane were prepared in this way. These can be

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa, Canada. Issued as Paper No. 51 on the Industrial Utilization of Agricultural Wastes and Surpluses and as N.R.C. No. 1577.

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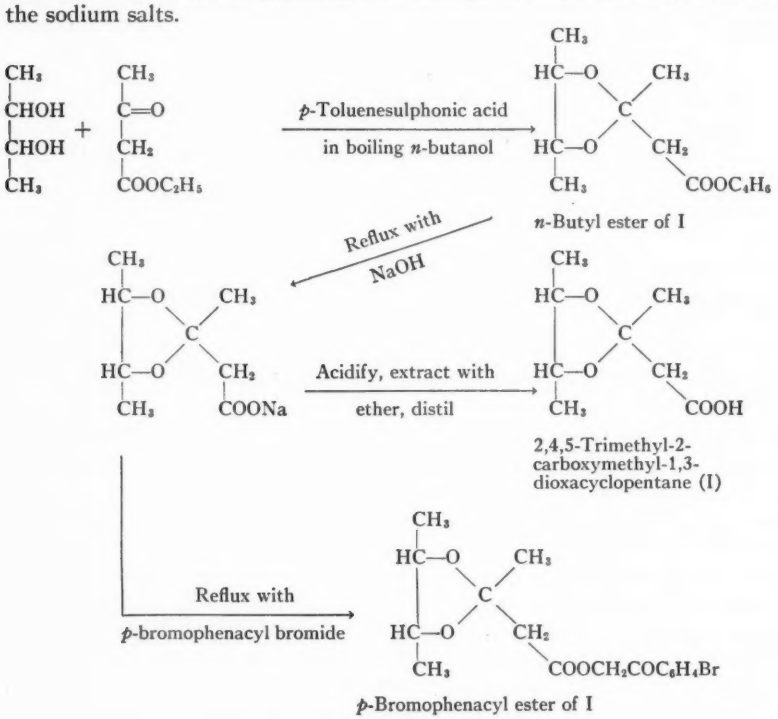
readily converted into the corresponding sodium salts by alkaline hydrolysis with sodium hydroxide. The free acids may be obtained from the sodium salts by acidification and extraction with ether. The yields are only 60 to 75%, probably because of hydrolysis of the dioxacyclopentane ring on acidification. The sodium salts can be converted to the crystalline *p*-bromophenacyl esters by refluxing with *p*-bromophenacyl bromide (75% yield based on butyl ester). These crystalline esters are very similar to each other in solubility and melting point and hence are not suitable for identifying the different isomeric 2,3-butanediols in a mixture. The above mentioned chemical transformations are shown in the following scheme. This has been realized with *levo*-, *dl*-, and *meso*-2,3-butanediol; all products have been purified and characterized except the sodium salts.



Experimental

Materials and Methods

The *l*-, *dl*-, and *meso*-2,3-butanediols were obtained by suitable purification of the 2,3-butanediols formed by bacterial fermentation as described below. The ethyl acetoacetate was obtained by redistilling the technical grade material obtained from the Certified Chemical Company. The *p*-bromophenacyl bromide, propionaldehyde, and *p*-toluenesulphonic acid (monohydrate) were Eastman chemicals, and the *n*-butanol, Merck's Reagent Grade.

The equivalent weights of the acids were determined by dissolving a weighed amount (2 gm.) in methanol and titrating to the phenolphthalein end-point with aqueous standard sodium hydroxide. The equivalent weights of the esters were determined by refluxing a weighed sample (2 gm.) with methanol and excess aqueous normal sodium hydroxide for two hours, allowing to cool overnight and then titrating to the phenolphthalein end-point with normal hydrochloric acid. Melting points were determined using an apparatus similar to that of Dennis and Shelton (2), which gives corrected melting points with an accuracy of 0.5° C. Bromine determinations were made using Umhoeffer's method (5), while carbon and hydrogen were determined by the well known method of Liebig. Refractive indices were determined by means of an Abbé refractometer.

levo-2,3-Butanediol

This isomer is easily obtained since *Aerobacillus polymyxa* produces it to the practical exclusion of the *meso-* and *dextro*-isomers (3). The material obtained from the Fermentations Pilot Plant, operated by this Division, was redistilled to give a colourless liquid, $[\alpha]_D^{25} = -12.84°$. This was used without further purification although it probably contains a small amount of water.

racemic-2,3-Butanediol

This can be made synthetically starting with *n*-butanol (6) but it is easier to prepare it by mixing *levo-* and *dextro*-2,3-butanediols prepared by fermentation. No organism is known that produces pure *dextro*-2,3-butanediol, but *Aerobacter aerogenes* gives a mixture of the *dextro-* and *meso*-isomers, which can be readily separated. This separation can be effected by direct distillation but since the isomers have boiling points only 3° to 4° C. apart it is advisable first to convert the mixture to the isomeric 2,2,4,5-tetramethyl-1,3-dioxacyclopentanes, which have boiling points separated by 8° to 9° C. This was done by condensing the 2,3-butanediol produced by *A. aerogenes*, $[\alpha]_D = +1.0$, with an equimolecular amount of acetone as previously described (4) for the *levo*-isomer. Owing to the relatively poor reaction obtained with the *meso*-isomer it is necessary to use 75 ml. of concentrated sulphuric acid per litre of diol in order to obtain two phases in a reasonable time. The top layer on distillation through a column packed with glass helices followed by redistillation through a Stedman column (about 24 theoretical plates) gave a fraction boiling between 109.5° and 110.5° C. This is chiefly *dextro*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane. After separation of a small intermediate fraction the *meso*-isomer was obtained boiling at 119° C. The total yield of crude ketals (top layer) was only about 25% owing to the poor reactivity of the *meso*-2,3-butanediol but one-quarter of this was the *dextro*-isomer. This shows the *meso*-isomer to be less reactive with acetone than the *dextro*. The observed rotation of this isomer was only +15.0° instead of +19.1° as expected by comparison with the *levo*-isomer (4). It is probable that the crude 2,3-butanediol used contained some of the *levo*-isomer, picked up in the

pilot plant when it was distilled through columns previously used for *levo*-2,3-butanediol. This view is substantiated by its rotation, which is a little lower than that expected.*

The fraction, $[\alpha]_D^{25} = +15.0°$, was mixed with sufficient *levo*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane to give an optically inactive solution. The racemic mixture thus obtained (598 ml.) was hydrolysed by refluxing with one litre of water containing 50 ml. of concentrated hydrochloric acid. The acetone was allowed to distil out through a 2 ft. column packed with glass helices. When the temperature reached 100° C. the residual solution was cooled, then neutralized with sodium hydroxide pellets to pH 4 to 5. The water was then distilled out and the residue separated from the sodium chloride by extraction with ether. Fractional distillation of the extract gave 340 ml. of *racemic*-2,3-butanediol boiling at 127° C. (124 mm.). This fraction had a refractive index of 1.4310 at 25° C. and a melting point of 7.0° to 7.5° C. These properties are in good agreement with those of the synthetic product (6). The yield on hydrolysis is about 95%.

meso-2,3-Butanediol

This can be prepared by hydrolysis of the *meso*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane obtained as described above. However, since *meso*-2,3-butanediol does not condense readily with ketones but reacts vigorously with aldehydes, it was decided to purify some of the crude *A. aerogenes* diol by reaction with propionaldehyde. One litre of the 2,3-butanediol, $[\alpha]_D = +1.0°$ was mixed with 800 ml. of Eastman's propionaldehyde and 5 ml. of concentrated hydrochloric acid added. The mixture heated spontaneously to 45° C. and two phases formed in a few minutes. It was stirred and allowed to cool overnight. The small lower layer was discarded; the top layer was washed with saturated sodium bicarbonate, filtered through anhydrous sodium sulphate and then distilled through a 2 ft. column packed with glass helices. Some diphasic azeotrope (40 ml. boiling at 89° C.) was obtained but the major fraction was a colourless liquid boiling at 125° to 133° C. with the observed rotation varying from + 1.0° to + 0.3°. The yield was 1400 ml. or 93%. This mixture of the *dextro*- and *meso*-2-ethyl-4,5-dimethyl-1,3-dioxacyclopentanes was carefully fractionated through a Stedman column and 480 ml. finally obtained with $[\alpha]_D = +0.06°$ and a boiling range 133.5° to 134.5° C. The lowest boiling fraction (126° to 127° C.) had $[\alpha]_D = +6.7°$. Most of the material was obtained as intermediate fractions. The fraction with the lowest rotation (415 ml.) was hydrolysed with dilute hydrochloric acid as described above for the *racemic* acetone derivative. Fairly pure *meso*-2,3-butanediol (250 gm.) was obtained as a white solid (m.p. 32° to 33° C.). The melting point of the highly purified diol is 34.4° C. (6).

* *The presence of dl-2,3-butanediol in this sample has recently been proved by isolation as the di-p-nitrobenzoate.*

Ethyl ester of levo-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

Ethyl acetoacetate (2 moles) and *levo*-2,3-butanediol (2 moles) were mixed, treated with 10 ml. of concentrated hydrochloric acid, and allowed to stand overnight. Then 200 ml. of ethyl ether was added to the diphasic product and the ethereal layer washed with 100 ml. of saturated sodium bicarbonate. After filtering through anhydrous sodium sulphate the ether extract was distilled through a column of glass helices. About 35 gm. of ethyl acetoacetate was recovered but the main fraction was a colourless liquid boiling at 114° C. (42 mm.). This proved to be the ethyl ester of the cyclic ketal formed between acetoacetic acid and *levo*-2,3-butanediol as expected. (Yield 48%). Calc. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97%; equiv. wt., 202.2. Found: C, 59.2, 59.3; H, 8.90, 8.85%; equiv. wt., 201, 203. $n_D^{25} = 1.4230$; $d_4^{25} = 1.0065$; $[\alpha]_D^{25} = -15.21°$. Molar refraction: calc., 51.26; found, 51.17.

A small amount (30 gm.) of a liquid boiling at 40° C. (300 mm.) with a camphor-like odour was obtained. This was probably the acetone derivative resulting from hydrolysis and decarboxylation of the ethyl acetoacetate. An attempt to obtain a high yield by using *p*-toluenesulphonic acid and removing the water by azeotropic distillation with benzene was unsuccessful. Owing to hydrolysis of the ester groups and possibly esterification with the diol, the yield obtained in this way was only 43%. However, a good yield could be obtained by carrying out the reaction in an excess of boiling butanol; in this case the main product is the butyl ester as shown next.

Butyl ester of levo-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

Ethyl acetoacetate (2 moles), *l*-2,3-butanediol (2 moles), and *n*-butanol (4 moles) were refluxed in an apparatus provided with a controlled take-off. The butanol was drawn off till the temperature of the vapour reached 115° C. A solution of 2 gm. of *p*-toluenesulphonic acid monohydrate in 500 ml. of butanol was added and 550 ml. then distilled off over a period of two hours as the temperature of the vapour rose gradually to 120° C. The reaction mixture was cooled overnight, then poured into a separatory funnel, washed with saturated sodium bicarbonate solution, filtered through anhydrous sodium sulphate, and fractionated through a column of glass helices. The butyl ester was the only product obtained in any appreciable quantity. (Yield 87%.) It is a colourless liquid boiling at 159° C. (58 mm.). Calc. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64%; equiv. wt., 230.3. Found: C, 62.4, 62.5; H, 9.45, 9.59%; equiv. wt., 228, 229; $n_D^{25} = 1.4270$; $d_4^{25} = 0.9781$; $[\alpha]_D^{25} = -13.39°$; molar refraction: calc., 60.47; found, 60.44.

Butyl ester of dl-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

racemic-2,3-Butanediol (2 moles) and ethyl acetoacetate (2 moles) were mixed with butanol (650 ml.) and *p*-toluenesulphonic acid monohydrate (2 gm.). During a period of 4½ hr., 610 ml. of butanol was distilled from the reaction mixture. It was cooled overnight, then washed, dried, and distilled as described above. A liquid boiling at 132° to 133° C. (100 mm.)

was obtained (35 gm.) but the main product was a liquid boiling at 157° C. (55 mm.). The former is probably the ethyl ester (yield 8%) while the latter was proved to be the butyl ester (yield 64%). The properties of the butyl ester were found to be as follows. Calc. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64%; equiv. wt., 230.3. Found: C, 62.5, 62.6; H, 9.62, 9.88%; equiv. wt., 227, 228. $n_D^{25} = 1.4269$; $d_4^{25} = 0.9790$. Molar refraction: calc., 60.47; found, 60.39.

Butyl ester of meso-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

Ethyl acetoacetate (2 moles) and *meso*-2,3-butanediol were condensed in boiling butanol as described above for the *levo*-isomer. The butyl ester of the cyclic ketal formed between acetoacetic acid and *meso*-2,3-butanediol was the only product obtained in any appreciable amount. (Yield 74%). It is a colourless liquid boiling at 164° C. (58 mm.). Calc. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64%; equiv. wt., 230.3. Found: C, 62.4, 62.5; H, 9.54, 9.60%; equiv. wt., 228, 229. $n_D^{25} = 1.4320$; $d_4^{25} = 0.9914$; molar refraction: calc., 60.47; found, 60.24.

levo-2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

This acid was obtained by saponification of its ethyl ester (0.5 mole) by refluxing with 50 ml. of methanol and 110 ml. of 5 *N* sodium hydroxide for one hour. After standing 16 hr. at room temperature the hydrolysate was adjusted to pH 10 and concentrated on a steam-bath to remove methanol. It was cooled, acidified with 10% excess of 10 *N* sulphuric acid and extracted with ether (twice), the extract washed with water, filtered through anhydrous sodium sulphate, and distilled. The acid was obtained as a colourless, viscous liquid with a faint camphor-like odour, boiling at 129° C. (5 mm.). (Yield 74%). It was redistilled through a short Vigreux column and its properties determined. Calc. for $C_8H_{14}O_4$: C, 55.15; H, 8.10%; equiv. wt., 174.2. Found: C, 55.1, 55.0; H, 8.08, 8.12%; equiv. wt., 175, 176. $n_D^{25} = 1.4352$; $d_4^{25} = 1.0856$; $[\alpha]_D^{25} = -18.40°$; molar refraction: calc., 42.04; found, 41.88.

dl-2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

This acid was obtained by saponification of its butyl ester (0.5 mole) by refluxing with 100 ml. of methanol and 110 ml. of 5 *N* sodium hydroxide for 1½ hr. The hydrolysate was cooled overnight, diluted with 500 ml. of water, acidified with 80 ml. of 7.5 *N* sulphuric acid and immediately extracted with 1200 ml. of ethyl ether used in three equal portions. The extract was washed once with water, filtered through anhydrous sodium sulphate, and distilled.

The chief product was 53 gm. of the crude acid (equiv. wt., 194) boiling at 127° C. (3 mm.). This contains some lower-boiling, neutral substance which was removed by fractionation through a short Vigreux column to give the pure acid boiling at 131° C. (6 mm.). (Yield 57%, calculated on acid in crude fraction.) Calc. for $C_8H_{14}O_4$: C, 55.15; H, 8.10%; equiv. wt., 174.2. Found: C, 55.1, 55.0; H, 8.10, 8.14%; equiv. wt., 177, 178. $n_4^{25} = 1.4350$; $d_4^{25} = 1.0795$; molar refraction: calc., 42.04; found, 42.11.

meso-2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

This acid was prepared by saponification of its butyl ester following the same procedure as that just given for the racemic mixture. It was obtained as a liquid boiling at 138° C. (5 mm.). The crude acid had an equivalent weight of 268 owing to the presence of some neutral substance. The analytically pure material obtained represented a yield of only 10% although a 68% yield of this acid was obtained (calculated on acid in high boiling fraction). Calc. for $C_8H_{14}O_4$: C, 55.15; H, 8.10%; equiv. wt., 174.2. Found: C, 55.1, 55.2; H, 8.10, 8.14%; equiv. wt., 176, 178. $n_D^{25} = 1.4415$.

p-Bromophenacyl Esters of the Isomeric 2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentanes

These were prepared from the corresponding butyl esters by saponification, followed by treatment of the sodium salt, thus obtained, with *p*-bromophenacyl bromide. The butyl ester (4 gm.) was treated with an excess of normal sodium hydroxide (20 ml.) and methanol (20 ml.), and refluxed for one hour. After allowing the reaction mixture to cool overnight it was titrated with normal hydrochloric acid till just acid to phenolphthalein. An equimolecular amount of *p*-bromophenacyl bromide was then added, the mixture refluxed for one hour, cooled, diluted with two volumes of water, and placed in a refrigerator. A greenish oil separated and then solidified. This was recrystallized from methanol to give yellowish crystals: m.p., 65° to 68° C. The yield at this stage was 70 to 75%. Two or three further recrystallizations from Skellysolve B gave pure colourless crystals. The *levo*-ester melts at 74.5° C. and the *dl*- and *meso*-ester both melt at 76° C. These compounds do not show much depression of the melting point when mixed; the last two when mixed in equal proportions give a mixture melting at 74° C., the lowest melting point observed. Calc. for $C_{16}H_{19}O_5Br$: C, 51.76; H, 5.16; Br, 21.53%. Found (*levo*-isomer): C, 51.7, 51.6; H, 5.19, 5.24; Br, 21.61, 21.55%. (*dl*-isomer): C, 51.5, 51.6; H, 5.28, 5.20; Br., 21.58, 21.52%. (*meso*-isomer): C, 51.7, 51.6; H, 5.28, 5.18; Br, 21.47, 21.51%.

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THE HYDROLYSIS AND POLYMERIZATION OF CYANOGEN CHLORIDE IN THE PRESENCE OF HYDROGEN CHLORIDE[1]

By A. B. Van Cleave[2] and H. E. Mitton[3]

Abstract

Cyanogen chloride reacts quantitatively with water in the presence of hydrochloric acid according to the equation: $CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$. As the percentage of hydrochloric acid is reduced towards zero, the rate of hydrolysis at 30° C. becomes exceedingly slow. The rate of hydrolysis, as indicated by the pressure increase, shows an increase with time which is particularly marked when the concentration of hydrogen chloride is less than 1%. This apparent autocatalytic effect is not due to the accumulation of solid ammonium chloride. A polymerization reaction, the rate of which is increased by the addition of dry hydrogen chloride, proceeds simultaneously with the hydrolysis reaction. Pure cyanogen chloride shows little or no tendency to polymerize at 30° C. Carbon dioxide has been shown to be quite soluble in liquid cyanogen chloride and an explanation has been suggested for the form of the pressure vs. time curves obtained in studying the acid catalyzed hydrolysis and polymerization of cyanogen chloride.

Introduction

It is well known that the stability of cyanogen chloride is greatly influenced by the presence of acid impurities (2). These impurities appear to have two effects: first, to catalyze the reaction of cyanogen chloride with water and, second, to catalyze the polymerization to cyanuric chloride $(CNCl)_3$ (1, 2, 5). The present work is concerned with the re-establishment of the products of the acid catalyzed hydrolysis and with a study of the factors affecting the rate of this reaction and the polymerization reaction.

It has been shown (4) that a considerable pressure of carbon dioxide is produced in closed systems consisting of cyanogen chloride, water, and small amounts of acid impurities. It is also known that part of the white solid that separates out from crude cyanogen chloride is ammonium chloride. These facts suggest that the over-all hydrolysis reaction might be represented by the equation:

$$CNCl + 2H_2O \longrightarrow CO_2 + NH_4Cl\ . \qquad (1).$$

This reaction can be shown to be entirely probable from a thermodynamic standpoint, the estimated equilibrium constant at 20° C. being of the order of 10^{48}.

Experimental

1. *Hydrolysis Experiments*

With the view of determining whether Equation (1) represented the over-all hydrolysis reaction, an apparatus (Fig. 1) was designed and constructed to follow the course of the reaction by measuring the pressure change and analysing the products.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., with financial assistance from the National Research Council of Canada.

[2] *Associate Professor of Chemistry.*

[3] *Graduate student. Holder at the time of a Bursary and Studentship under the National Research Council of Canada.*

Crude cyanogen chloride (American Cyanamid Company) was filtered to remove polymer and solid ammonium chloride, and then purified by fractional crystallization (6). Liquid cyanogen chloride was about 80% frozen and the remaining liquid poured off. The solid was then melted and the process repeated, until a product showing a constant freezing point of $-6.9°$ C. was obtained. Cyanogen chloride purified in this way proved to be quite stable over considerable periods of time. The purified liquid in *A* (Fig. 1) was allowed to vaporize into the previously calibrated and evacuated measuring vessel, *B*. Assuming that the vapour of cyanogen chloride obeys the ideal gas laws at 20° C. and pressures less than 1 atm., the amount of cyanogen chloride transferred from *A* to *B* could be calculated. When sufficient

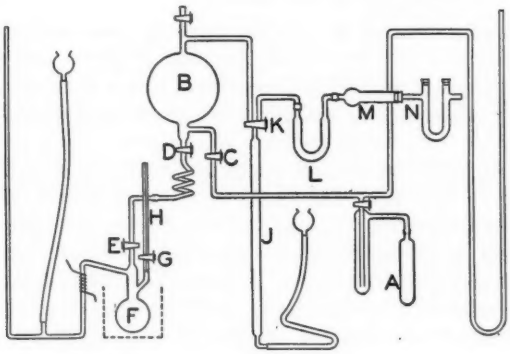

FIG. 1. *Diagram of apparatus.*

cyanogen chloride vapour had accumulated in *B*, stopcock *C* was closed and *D* and *E* opened to allow the vapour to freeze out in the evacuated reaction vessel, *F*, which was immersed in a dry ice – acetone freezing mixture. The amount of cyanogen chloride remaining in the vessel *B* was negligible as its vapour pressure at $-78°$ C. is less than 1 mm. of mercury. When the transfer was complete the stopcocks *D* and *E* were closed (*E* being clamped) and the reaction vessel and attached manometer removed and placed in a constant temperature bath. When equilibrium was established, the vapour pressure was noted as an additional check on the purity of the cyanogen chloride. The reaction vessel was then cooled until the vapour pressure of the cyanogen chloride was somewhat less than atmospheric, when the desired amount of standard hydrochloric acid solution was admitted through the tap, *G*, from the calibrated capillary burette, *H*. After mixing the reactants by shaking, the reaction vessel was re-immersed in the constant temperature bath and the course of the reaction followed by noting the pressure at intervals. In all cases the pressure increased up to a maximum where readings were discontinued in the initial experiments.

The next step was to analyse the products qualitatively and quantitatively. Condensable vapours in the reaction vessel were frozen out with a dry ice – acetone bath. The reaction vessel was again attached to the evacuated measuring bulb, *B*, and stopcocks *D* and *E* opened, allowing the uncondensed gases to flow until equilibrium was attained. Stopcock *D* was then closed and the gas in the measuring chamber analysed. The gas in *B* still contained a small amount of cyanogen chloride which could be detected by its odour and lachrymal property. Some of the gas was bubbled through a saturated barium hydroxide solution, and a heavy white precipitate resulted. This precipitate was filtered out, washed and dried, and analysed gravimetrically for barium. It yielded 68% of barium, whereas the theoretical value for barium carbonate is 69.5%. This indicated that a considerable amount of carbon dioxide had been formed during the reaction.

A quantitative analysis of the gas was done by attaching a mercury filled, calibrated gas burette, *J* (Fig. 1), to the bulb, *B*, by the three-way tap, *K*. This made it possible to withdraw measured portions of the gas and transport them to the gas absorber, *L*, which contained dilute (chloride free) sodium hydroxide solution. Attached to the gas absorber was a calcium chloride tube, *M*, to absorb any water that might be lost from the sodium hydroxide solution during the absorption process. The tubes *L* and *M* were weighed before and after absorption. A tube, *N*, containing a mixture of soda lime and calcium chloride served to protect the absorption train from atmospheric carbon dioxide and water vapour. When absorption was complete the solution was transferred to a volumetric flask and diluted to 500 ml. Portions of the solution were analysed for chloride by the Vohlhard method. The chloride arose from two sources: first, cyanogen chloride that had not been completely removed by the freezing-out treatment, and second, from the hydrogen chloride added to the system. Since it was not possible to estimate the amount of the latter present, the calculations were made on the basis that all the chloride arose from cyanogen chloride. The amount of carbon dioxide produced was then calculated by difference.

The excess of unreacted cyanogen chloride in the reaction vessel, *F*, was allowed to escape. There remained a white residue that could be divided into two portions, one soluble in chloroform and the other in water. After several extractions with chloroform the remaining residue was dissolved in water. This solution gave good qualitative tests for NH_4^+ and Cl^- ions. A Kjeldahl analysis on a dry portion of this residue gave a result in close agreement with that expected from ammonium chloride. Hence it was concluded that ammonium chloride was also a product of the hydrolysis reaction.

The results of a number of typical experiments are given in Table I. The weight of water present was calculated from the known volume of standard hydrochloric acid that was added. The amounts of ammonium chloride and carbon dioxide to be expected if all the water reacted according to the equation $CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$ are contrasted with the amounts of these substances actually produced in each experiment. In every case the amount

of product found was less than that theoretically expected, but the differences are believed to be within the limits of experimental error of the method. These results indicate that the reaction between cyanogen chloride and water in the presence of hydrogen chloride is satisfactorily represented by Equation (1).

TABLE I

HYDROLYSIS EXPERIMENTS AT 20° C.

(Weights are in grams)

Expt.	Reactants		Products			
	CNCl	H_2O	NH_4Cl (calc.)	NH_4Cl (obs.)	CO_2 (calc.)	CO_2 (obs.)
4	6.34	0.3862	0.574	0.537	0.482	0.447
7	6.34	0.3838	0.570	0.534	0.469	0.461
8	6.34	0.3838	0.570	0.523	0.469	0.439
9	6.34	0.3838	0.570	0.533	0.469	0.436

As previously mentioned, the pressure increased to a maximum in all experiments, at which time the initial experiments were discontinued. On further investigation it was found that after the maximum pressure had been reached, there followed a decrease in pressure with time. Consequently, some experiments were allowed to proceed until no further pressure change occurred (approximately 21 days at 20° C.). The results of typical experiments are shown in Fig. 2. Experiment 9, at 20° C., was in progress for 20.3 days

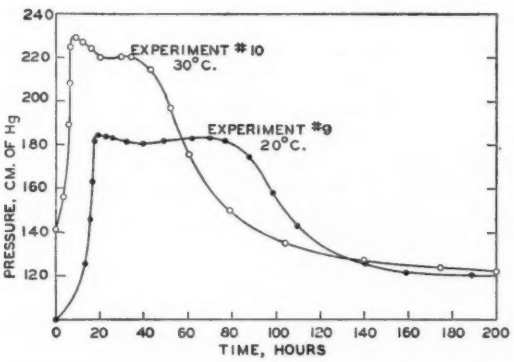

FIG. 2. *Pressure vs. time curves for the hydrogen chloride catalyzed hydrolysis and polymerization of cyanogen chloride at 20° and 30° C.*

and the final steady pressure was 114.7 cm. of mercury. If the hydrogen chloride was not used up in the reaction, its partial pressure at the end of the reaction could be calculated. The pressure of carbon dioxide produced could also be calculated from the known amount of water added and the known

volume of the apparatus. If, at the end of the reaction each of these substances was exerting its own partial pressure, and there were no other substances present with appreciable vapour pressures, the final pressure to be expected in the above experiment was calculated to be 117 cm. of mercury, which is in good agreement with the figure 114.7 cm. obtained.

When these experiments were terminated, all the liquid cyanogen chloride appeared to be gone but, in addition to the ammonium chloride formed, there was a considerable amount of a yellow-white crystalline solid. This substance was soluble in chloroform and was believed to be polymerized cyanogen chloride (i.e., cyanuric chloride). The chloroform solution of the polymer was allowed to evaporate to dryness and the amount of the polymer determined by weighing. The results for the amounts of ammonium chloride, carbon dioxide, and cyanuric chloride produced in several experiments are given in Table II. In Experiments 7 to 10, inclusive, a hydrochloric acid solution containing 0.0958 gm. of hydrogen chloride and 0.3838 gm. of water was added to 6.34 gm. of cyanogen chloride, giving a total weight of reactants of 6.718 gm. It will be observed from this table that a fairly satisfactory balance of materials was obtained.

TABLE II

HYDROLYSIS AND POLYMERIZATION PRODUCTS AT 20° C.

(Weights are given in grams)

	NH_4Cl	CO_2	$(CNCl)_3$	Total	Loss
Calc. from Equation (1)	0.570	0.469	5.679	6.718	—
Observed in Expt. 7	0.534	0.461	5.253	6.248	0.470
8	0.523	0.434	5.297	6.254	0.464
9	0.533	0.436	5.561	6.530	0.188
10[1]	0.541	0.466	5.666	6.673	0.045

[1] *Experiment 10 was carried out at 30° C. and the results are shown in Fig. 2 for comparison with Experiment 9. The shapes of the two curves are similar, but the maximum pressure was reached in 6.6 hr. at 30° C., whereas about 18 hr. were required at 20° C. Thus, the rate of this phase of the reaction was increased somewhat more than two and a half times for a 10 degree rise in temperature.*

An examination of the pressure vs. time curves (Fig. 2) indicates that the rate at which the pressure increases in the initial stages increases with time as if there were an autocatalytic effect. An experiment was carried out to ascertain whether solid ammonium chloride would act as an autocatalyst. This experiment was in all respects similar to Experiment 10 (Table II) except that 0.555 gm. of solid ammonium chloride was added to the reaction vessel before the reactants were admitted. However, the time for the maximum pressure to be reached was 6.6 hr., the same as in Experiment 10, thus indicating that the presence of solid ammonium chloride has little or no effect on the rate of the hydrolysis reaction.

A number of experiments were performed to study the effect of varying amounts of hydrogen chloride on the acid catalyzed hydrolysis of cyanogen chloride. The procedure in each case was the same; 10.25 gm. of cyanogen chloride were transferred to the reaction vessel and a known volume of standard acid added. The amount of hydrogen chloride in each experiment was controlled by the concentration of the solution used. The time for the completion of the hydrolysis reaction was taken as the time at which the first maximum in the pressure vs. time curve was reached. Fig. 3 is a graph of

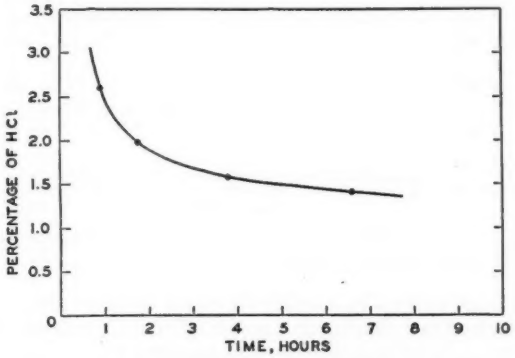

FIG. 3. *Weight per cent of hydrogen chloride vs. the time for complete reaction of water with cyanogen chloride at 30° C.*

the weight per cent of hydrogen chloride used vs. the time of complete reaction of the water at 30° C. These results show that the reaction is rather slow at 30° C. if the percentage of hydrogen chloride is less than 1, but the rate increases very rapidly as the hydrogen chloride concentration is increased above 1.5%. However, even traces of hydrogen chloride in cyanogen chloride could result in dangerous pressure increases over a period of time if there was any appreciable amount of water present. An experiment was started in which only pure cyanogen chloride and water were present. An extremely slow pressure increase occurred over a period of four weeks. Whether this was due to a direct reaction between cyanogen chloride and water or whether it was due to catalysis by traces of acid, it is not possible to say.

2. *Polymerization Experiments*

A series of experiments were performed to study the effect of adding dry hydrogen chloride to cyanogen chloride at 30° C. Known amounts of pure cyanogen chloride and hydrogen chloride (generated by the action of sulphuric acid on sodium chloride and dried by passage through phosphorus pentoxide) were introduced into reaction vessels similar to those used in the study of the acid catalyzed hydrolysis. The progress of the reaction was followed by noting the pressure changes.

The pressure vs. time curves of a series of polymerization experiments are shown in Fig. 4, together with that for a blank (i.e., no hydrogen chloride present). In all such blank experiments there was no change in the vapour

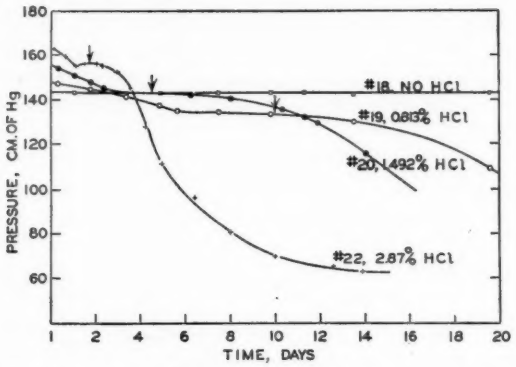

FIG. 4. *Pressure vs. time curves for the polymerization of cyanogen chloride with varying weight percentages of dry hydrogen chloride at 30° C.*

pressure of cyanogen chloride nor did any solid polymer separate out. One of these experiments extended over a period of six weeks, indicating that pure, dry cyanogen chloride is reasonably stable at 30° C.

When the reaction vessels, to which hydrogen chloride had been added, were opened, they were found to contain a white crystalline solid and a small amount of a yellow liquid along with the hydrogen chloride that had been added. The greater the amount of hydrogen chloride that had been added, the shorter was the time required for polymerization of a given amount of cyanogen chloride. In the reactions involving larger amounts of hydrogen chloride, more of the yellow liquid was formed. It was also noticed that, in experiments in which polymerization had taken place slowly (smaller quantities of hydrogen chloride), fewer but larger crystals resulted. In one experiment a large crystal, approximately 1 by $\frac{3}{4}$ in., was formed. All the cyanogen chloride had apparently been used up by the time the tests were terminated because it could not be detected by its odour or its lachrymating effect. The odour of the products was similar to that which accompanies crude acetamide. Some of the larger crystals of polymer were washed with chloroform, dried, and found to melt at 142.5° C. This is 2.5 degrees lower than that reported by Whitmore (5) for cyanuric chloride. It was noted that the solid tended to sublime at temperatures in the vicinity of the melting point.

In the experiments shown in Fig. 4, the vapour pressure of each of the cyanogen chloride – hydrogen chloride mixtures was greater than the vapour pressure of pure cyanogen chloride, but the increase in pressure was approximately half as much as would be expected if the hydrogen chloride was insoluble in cyanogen chloride. This indicates that the solubility of hydrogen chloride in cyanogen chloride is appreciable.

The time for complete polymerization of the liquid phase was taken as the time that the pressure began to decrease from a fairly constant value (shown by arrows in Fig. 4), the decrease being due to polymerization of cyanogen chloride remaining in the gas phase (see discussion). The fact that crystals of the polymer formed on parts of the apparatus not in contact with liquid cyanogen chloride indicates that polymerization takes place directly from the vapour phase. Fig. 5 is a plot of the time required for complete liquid phase

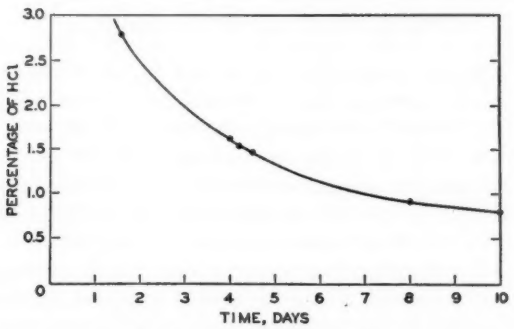

FIG. 5. *Weight percentage of hydrogen chloride vs. the time required for complete liquid phase polymerization of a given quantity of cyanogen chloride at 30° C.*

polymerization of a given quantity of cyanogen chloride vs. the percentage of hydrogen chloride. Although a direct relation between the concentration of hydrogen chloride and the rate of polymerization does not appear to exist, it is evident that the rate does increase rapidly as the concentration of hydrogen chloride is increased above 1%.

3. *Solubility Experiments*

A series of experiments were carried out to determine the extent to which carbon dioxide dissolves in liquid cyanogen chloride. The object of this part of the work was to obtain data that could be used to determine the correct pressure increase in the hydrolysis experiments. An apparatus was designed and constructed to measure the quantity of gas required to saturate a quantity of initially gas-free solvent. Unfortunately, the results obtained were not sufficiently reproducible to warrant publication. In an attempt to check the method and apparatus, experiments on the solubility of carbon dioxide in water were done, but the same inconsistencies appeared. The main difficulty was that the solubility, expressed as volume of gas dissolved per unit volume of solvent at 20° C., fell off rapidly for gas pressures less than 30 cm. of mercury. For gas pressures of about 50 cm. of mercury, results in reasonable agreement with those cited in the literature (3) were obtained, but the reproducibility was not good. The same type of difficulty was encountered in

experiments on the solubility of carbon dioxide in cyanogen chloride. It can be stated, however, that at gas pressures above 30 cm. of mercury, the solubility of carbon dioxide in liquid cyanogen chloride is of the order of 8 ml. per ml. of solvent at 20° C.

Discussion

The reaction of cyanogen chloride with water in the presence of hydrogen chloride has been shown to proceed quantitatively according to the equation:

$$CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl.$$

The reaction probably takes place in several steps, the hydrogen chloride acting as a catalytic agent in one or more of these steps. The reaction has been shown to be extremely slow in the absence of hydrogen chloride.*

The pressure vs. time curves for the hydrogen chloride catalyzed polymerization (Fig. 4) all have the same general shape, and the following is a suggested explanation. When the reaction is first initiated the total pressure is that due to the vapours of the pure cyanogen chloride – hydrogen chloride solution. As polymerization takes place the vapour pressure of the cyanogen chloride is reduced because the polymer formed is soluble in cyanogen chloride to some extent. This explains the first gradual decrease of total pressure with time. A point will be reached, however, where the cyanogen chloride becomes saturated with polymer and further polymerization leads to a separation of solid cyanuric chloride. Under these conditions the vapour pressure of a simple solvent would assume a fixed value which would persist until all the liquid had polymerized. However, this case is complicated by the presence of dissolved hydrogen chloride, and, as polymerization of the cyanogen chloride proceeds, some of the hydrogen chloride will be forced out of solution and may cause the pressure to rise again as in Experiment 22, Fig. 4. In some cases this effect was more gradual and did not result in a second maximum in the pressure vs. time curve. When all the liquid cyanogen chloride has polymerized, the total pressure begins to decrease slowly to its final value as the remaining cyanogen chloride vapour itself polymerizes.

The graphs of Fig. 2 show the characteristic double maxima that usually occur in the pressure vs. time curves for the acid catalyzed hydrolysis. The initial increase in pressure, to the first maximum, is due to the formation of carbon dioxide. Polymerization of cyanogen chloride probably takes place simultaneously with the hydrolysis. When the water has completely reacted, polymerization of the remaining cyanogen chloride continues until it is all transformed. Thus the explanation of the general form of the curves (Fig. 2), after the first maximum is reached, is similar to that suggested above with reference to Fig. 4, provided that the cyanogen chloride is not yet saturated with polymer. The only essential difference is that carbon dioxide and ammonium chloride are present along with hydrogen chloride, cyanogen

* *Additional experiments on the kinetics of this reaction in dioxane solution are now in progress in this laboratory.*

chloride, and cyanuric chloride. The presence of carbon dioxide will affect the polymerization curve by a displacement along the pressure axis and may also contribute to the occurrence of the second maximum as it is forced out of solution by a decrease in the amount of solvent. When all the cyanogen chloride has polymerized the pressure has decreased to a value that was found to be the sum of the partial pressures of the carbon dioxide and hydrogen chloride.

An examination of the results indicates that the rates of polymerization with and without the presence of water were quite different, the rate being considerably greater in the experiments in which water was initially present. For example, in Experiment 10 (Table II and Fig. 2) the time for complete liquid phase polymerization was about 31 hr. after the initiation of the reaction. In this case, 6.335 gm. of cyanogen chloride and 0.0958 gm. of hydrogen chloride were used, i.e., the mixture was 1.44% hydrogen chloride if the reaction is considered only from the standpoint of cyanogen chloride and hydrogen chloride. Referring to the graph in Fig. 5, the time required for the polymerization of 10.25 gm. of cyanogen chloride containing 1.44% of dry hydrogen chloride was 109 hr. In the hydrolysis experiment (Experiment 10), 0.640 gm. of cyanogen chloride reacted with water, leaving 5.695 gm. available for polymerization. If this amount had polymerized at the same rate as it does in the presence of dry hydrogen chloride, 60.5 hr. would have elapsed before complete liquid phase polymerization. Actually, however, this stage was reached in only 31 hr., making it very evident that the rates under the different conditions are not at all comparable. A possible explanation for this is that the amount of hydrogen chloride in actual contact with the cyanogen chloride may be greater in the hydrolysis experiments, as all the acid originally added mixed with the cyanogen chloride, whereas, in the polymerization experiments, the hydrogen chloride was added as a gas which did not all dissolve in the cyanogen chloride.

With the experimental method used it is not possible to calculate rate constants for the hydrolysis reaction, as an interpretation of the pressure increase is complicated by factors such as the solubility of carbon dioxide in the cyanogen chloride and by the polymerization of cyanogen chloride.

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THE ADSORPTION OF ALIPHATIC ACIDS ON ACTIVATED CHARCOALS[1]

By R. U. Lemieux[2] and J. L. Morrison[3]

Abstract

The adsorptions of acetic, propionic, butyric, and valeric acids from aqueous solutions on a series of coconut charcoals of different degrees of activation were determined. For purposes of interpretation the numbers of millimoles adsorbed per gram of charcoal were compared for pairs of acids. Unimolecular adsorption of the acids is indicated. Surface areas of the charcoal series were estimated. They range from 130 to 625 sq. m. per gm. of charcoal, depending on the adsorbate used and the degree of activation of the charcoal. Some insight into the activation process is given.

Introduction

Some knowledge of the internal structure of activated charcoal can be obtained by measurements of the surface area at different degrees of activation.

Many attempts have been made to measure the surface area of charcoal by adsorption from solutions. Generally these have consisted in determining the adsorption isotherm for a solute in a suitable solvent. By extending the concentration range until the amount of solute adsorbed per gram of charcoal appears to be independent of concentration, it is assumed that saturation of the charcoal–liquid interface by the solute is reached. If the size and orientation of the adsorbed molecules and the thickness of the adsorbed layer are known, the specific surface area of the adsorbent can be calculated.

This paper presents some experimental results which indicate that the adsorption of aliphatic acids (acetic to valeric) at the charcoal–water interface is unimolecular, and that activated coconut charcoal has multi-sized pores with a pore size distribution dependent on the degree of activation.

The adsorption of the lower normal aliphatic acids from aqueous solutions on various types of charcoal have been determined many times. For instance, Linner and Gortner (5) determined the adsorption of several organic acids on Norit charcoal. What is unique in the results that follow is that the charcoals employed were a series consisting of the same charcoal at different stages of activation.

Experimental

The coconut shell charcoal samples were obtained from the Standard Chemical Co. Ltd., Montreal. They consisted of a series of eight samples removed from the steam activator at approximate intervals of 24 hr. The eighth sample was nearly completely activated. Further steam treatment of the charcoal beyond Charcoal 8 causes a decrease in activity. This was shown experimentally in this laboratory for a similar charcoal series. In

[1] *Manuscript received January 29, 1947.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alta.

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Table I are given some data on these samples. The volume activities and mercury densities were determined by Dr. J. C. Arnell of Ottawa. The nitrogen adsorption measurements were made by M. Nay (7) using the method of Brunauer, Emmett, and Teller (2).

TABLE I

DATA ON THE COCONUT CHARCOALS

Sample No.	Volume activity[1]	Mercury density,[2] gm./cc.	Nitrogen adsorbed,[3] v_m millimoles/gm.
1	1.5	1.140	4.88
2	3.8	1.103	5.92
3	6.2	1.086	8.42
4	11.4	1.036	9 79
5	11 6	1.034	10.18
6	17.3	0.969	11.06
7	21.7	0.933	12.58
8	24.6	0.896	—

[1] *Volume activity—an empirical test based on carbon tetrachloride retentivity.*
[2] *Mercury density—charcoal density in mercury at ½ atm. pressure (3, p. 112).*
[3] *Nitrogen adsorption, v_m, is the volume of adsorbate that covers the surface with a monolayer.*

The acetic, propionic, butyric, and valeric acids were chemically pure grade, from Eastman Kodak Company. In some cases they were refractionated and the constant boiling fractions used. The sodium hydroxide solutions were free from carbon dioxide and standardized with potassium acid phthalate.

A weighed sample of charcoal (0.25 to 2.0 gm., corrected for moisture content) was placed in a 250 ml. Erlenmeyer flask. Acid solution (100 ml.) was accurately pipetted into the flask. To attain equilibrium, the flask was shaken for one-half hour and then allowed to stand for various lengths of time depending on the adsorbate.

A portion (25 ml.) of the equilibrium mixture was titrated with standardized sodium hydroxide solution, using phenolphthalein indicator. In this way the equilibrium concentration and the amount of acid adsorbed per gram were determined. Some experiments were made in a bath thermostatically controlled at 25.0 ± 0.1° C., and some at room temperature (23° to 27° C., summer 1943). No difference in the amount of saturation adsorption was found. Consequently room temperature was used in these experiments.

The effect of evacuation of the charcoal, both before and after contact with the solution, was tested. These tests gave the same results as the experiments without evacuation.

Results

The acids used in these experiments exhibited the typical Langmuir curve when the amount adsorbed per gram was plotted against the concentration in the substrate. The maximum amounts of the various acids adsorbed on charcoals of different degrees of activation are given in Table II. Maximum adsorption occurs at about 2.0 *N* for acetic, 0.5 *N* for propionic, 0.35 *N* for butyric, and 0.25 *N* for valeric acid.

The experimental results were interpreted by comparing the maximum adsorptions of the various acids with one another. This is done in Figs. 1, 2, and 3. Here the number of millimoles per gram (x/m) for each acid are plotted against the x/m of another particular acid, for each charcoal.

TABLE II

MAXIMUM MILLIMOLES OF ACID ADSORBED PER GRAM OF CHARCOAL

Charcoal No.	Acetic	Propionic	Butyric	Valeric
1	2.15	1.63	1.24	0.88
2	2.55	2.04	1.66	1.31
3	2.85	2.47	2.06	1.75
4	3.22	2.91	2.63	2.40
5	3.25	2.93	2.74	2.41
6	3.70	3.46	3.43	3.18
7	4.00	3.75	3.84	3.66
8	Insufficient charcoal	3.96	4.25	4.01

Some time studies were also made. The times required to reach equilibrium at saturation concentrations were measured by D. M. Miller (6) for Charcoal 3 (low activation) and Charcoal 7 (high activation). They are given in Table III.

TABLE III

EQUILIBRIUM TIMES OF ADSORPTION FROM SOLUTION ON CHARCOALS

Adsorbate	Initial concentration, M	Time, hr.	
		Charcoal 3	Charcoal 7
Acetic acid	2.3	16	4
Propionic	0.53	16	4
Butyric	0.37	10	6
Valeric	0.24	8	10
Caproic	0.039	4	16

Discussion

Surface Area

The adsorption measurements give consistent correlations with the volume activities, mercury densities, and nitrogen adsorptions.

In general, the charcoal density determined with mercury is very low compared with the absolute density of charcoal. Mercury does not penetrate the small pores of the charcoal. Therefore mercury density is an inverted measure of the pore volume. The acid adsorption increases as the mercury density decreases. Probably the processes of increase in pore volume and of increase in surface area occur simultaneously.

The charcoal surface areas presented to various acids have been calculated on the assumption of a unimolecular adsorption layer and vertical orientation of the adsorbate molecules. These are given in Table IV. In these calculations, an adsorbate area of 24.3Å² per molecule was used, as this area was found for some of these acids at the water–air and water–benzene interfaces (8, p. 50). In addition the surface areas presented to nitrogen have been calculated on the assumption of solid packing of the nitrogen molecules.

TABLE IV

SURFACE AREAS AVAILABLE TO ACID ADSORBATES

Sample	Area, sq. m. per gm.				
	Acetic	Propionic	Butyric	Valeric	Nitrogen[1]
1	316	240	182	128	408
2	375	300	244	193	495
3	419	363	303	258	704
4	474	428	387	353	819
5	478	431	403	354	852
6	544	509	505	468	924
7	589	551	565	538	1052
8	—	583	625	590	—

[1] *Calculated from v_m on the basis of a nitrogen molecular area of 13.8Å² (solid packing).*

The areas found with the acids were from about 130 to 625 sq. m. per gm., depending largely on activation and to a lesser degree on the size of the adsorbate molecule. A comparison of these areas with those obtained with nitrogen seems to indicate that the acids adsorb on only part of the charcoal surface. A comparison with the areas obtained by Fineman, Guest, and McIntosh (3) with nitrogen on a different charcoal series indicates that the two series of charcoal are similar.

Unimolecular Adsorption

Figs. 1, 2, and 3 are plotted on the basis of Table II. For comparison the straight line cutting the origin at 45° is added to each figure. This line represents the amount of acid adsorbed when plotted against itself—that is, against the same number of molecules adsorbed on the same surfaces. It will be noted that all pairs approach the slope of unity, particularly in the region of low activation. The intercept on the abscissa indicates the extra number of millimoles of the smaller molecule adsorbed. This extra number is approximately the same for consecutive pairs of acids. The validity of the extrapolations in Figs. 1, 2, and 3 may be questionable. However, the authors have no reason, either from experimental results or from logic, to doubt that such extrapolations are valid.

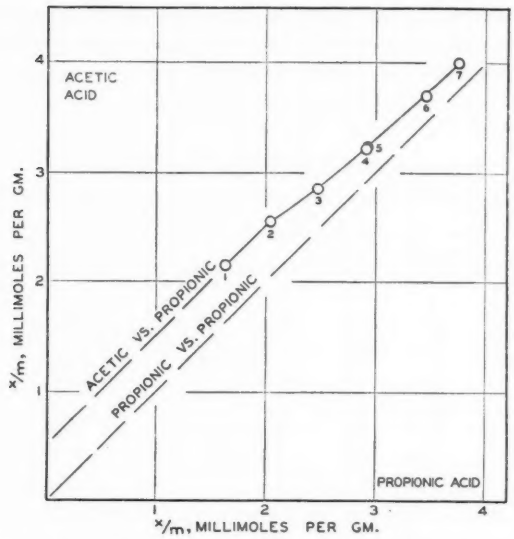

FIG. 1. *Comparison of acetic with propionic acid for charcoal series.*

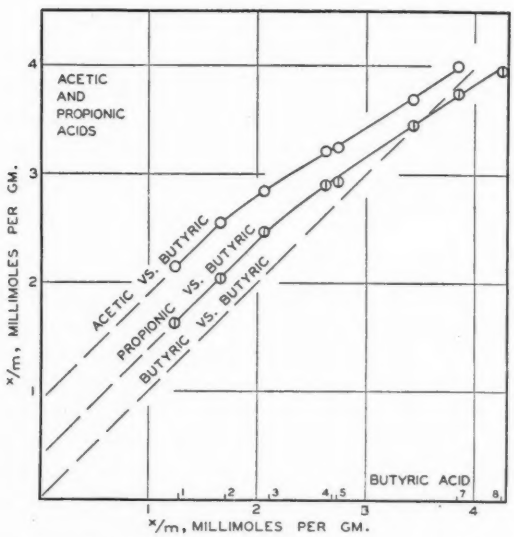

FIG. 2. *Comparison of acetic and propionic with butyric acid for charcoal series.*

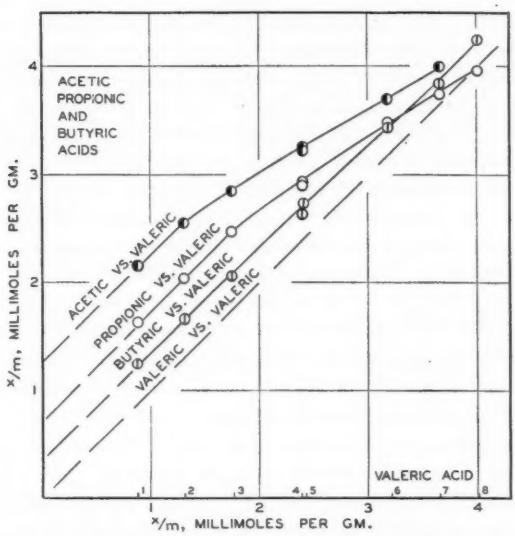

FIG. 3. *Comparison of acetic, propionic, and butyric with valeric acid for charcoal series.*

The intercepts may be interpreted as a measure of the extra relative area of the pore walls available to the smaller molecules. The fact that the lines are at a 45° angle at lower activations is interpreted as indicating unimolecular adsorption.

An alternative explanation is possible, based on the assumption that the same area is available to all the molecules. One might then suggest further that the acid molecules lie flat on the charcoal surface, covering areas proportional to their lengths. However, this conception is contradictory to two general facts. First, coconut charcoal usually presents different surface areas to different adsorbates (1), and second, the aliphatic acids tend to orientate vertically at saturated water–air interfaces (4, p. 1886).

Pore Size and Size Distribution

Assuming that charcoal is a complex network of pores of various diameters, and that the aliphatic acids adsorb unimolecularly from solution at the water–charcoal interface, it is possible to estimate the average thickness of the pore walls. For Charcoal 3 this is about 3 carbon atoms, a thickness of about 4.5Å. Probably many walls are thicker, and many thinner than this.

An estimate of the average pore diameters will be made in a later paper. However, some idea of pore size distribution may be gained by examining Figs. 1, 2, and 3. The adsorbed films are in dynamic equilibrium with the outside solution. Therefore, though the adsorbate molecules may have a common cross-sectional area, they present to the pore openings an average size which depends largely on their length. Acetic acid will reach pore walls

that valeric cannot. This is supported by the fact that the intercepts in the figures are in the consistent direction. The further fact that these intercepts are approximately proportional to the increase in chain lengths of the adsorbate molecules indicates an even distribution of the pore sizes for the less activated Charcoals 1 to 3. However, the nitrogen areas of the charcoals indicate that there are a large number of very small pores not reached by these acids.

Thus, it is quite possible to account for the results on the basis of unimolecular adsorption and, particularly for the less activated charcoals, of an even distribution of pore sizes. This distribution refers to sizes of the same order of magnitude as the sizes of the adsorbate molecules.

Orientation of the Adsorbate Molecules

It has been assumed that the molecular orientation is vertical in the saturated acid films at the water–carbon interface. The results provide some evidence for the validity of this assumption.

While the less activated Charcoals 1, 2, and 3 show distinct and parallel differences in the number of moles of acid adsorbed, the more activated Charcoals 6, 7, and 8 tend towards identity in the number of moles of acids adsorbed. Changes in porosity, in which the dimensions of the pores are similar to the dimensions of the acid adsorbates, account for the behaviour of the less activated charcoals. Eventually, however, the activation process must give rise to sufficiently large pores to permit all acids to enter most of the internal surface. This is the probable explanation for the fact that the four acids from acetic to valeric give about the same number of moles adsorbed for Charcoals 7 and 8. Differences in the packing of the adsorbed molecules may account for the fact that Charcoals 7 and 8 adsorb more butyric acid than propionic acid. Similarly Charcoal 8 adsorbs more valeric acid than propionic acid.

A larger proportion of pores accessible to all these acid molecules would be expected as activation proceeds. This expectation, together with the fact that the number of moles adsorbed approaches identity at higher activations, suggests a similar area being occupied by each molecule (of the acid series). This indicates vertical orientation, the common cross-section being either the methyl or carboxyl groups. The latter, being the larger, is considered the determining one. Presumably in a saturated film, the acid molecules are oriented perpendicularly to the carbon surface, with the hydrocarbon end towards the carbon and the carboxyl end towards the solution.

Since the amount adsorbed per gram of charcoal can be determined with an accuracy of 1% or better, the accuracy of the determination of the surface areas of charcoal by this method is limited by the accuracy to which the area covered by each molecule is known, and, of course, by the accessibility of these adsorbates to the internal surface.

It is well to remember that, when pore radii and adsorbate molecules are similar in size, the meaning of *area* as measured by these adsorbates is somewhat uncertain. This point will be considered in a later paper.

Activation

The activation process for coconut shell charcoal can be elucidated somewhat by an examination of the results and calculations.

The process appears to involve an increase in the total pore volume. At the same time, for charcoals up to No. 3, the pore size distribution is fairly constant and regular for pore sizes of the same order as the sizes of the molecules of the acids used.

However, as activation proceeds beyond the stage of that of Charcoal 3, this constant progressive development deteriorates. The rate of increase of the number of pores accessible to molecules of the size of those of acetic and propionic acids decreases compared with that of the number of the size accessible to butyric. This is shown by the fact that the curves for acetic and propionic acids plotted against valeric, Fig. 3, take a downward trend while that for butyric remains parallel. It would appear that pores of the size accessible to butyric and valeric acid molecules are forming at the expense of pores of the size accessible to molecules of propionic and acetic acids. This process continues until the stages of activation of Charcoals 7 and 8 are reached. In Charcoal 6, for instance, all pores accessible to propionic are accessible to butyric, but not yet to valeric. Acetic acid, with the smallest molecule, has in all these charcoals access to some pores that are inaccessible to the other acids.

An increase in the average pore radius with increased activation is implied in this paper. This is corroborated by McIntosh and his collaborators (3, p. 117) who found an increase in pore size with activation for a similar charcoal series. In their case, they calculated the pore radii from water vapour adsorption data by the Cohan equation.

The maximum of the activation process would probably occur when further treatment (steam activation) would decrease the surface area, that is, when a net gain in surface area no longer would obtain by sacrificing small pores for large ones. That this is so was shown for samples of another coconut shell charcoal, prolonged activation of which resulted in a decrease in the amount of acid adsorbed from solution.

Further confirmation of the ideas presented in this paper with respect to porosity changes during the activation process is given by the fact that the times to reach equilibrium for Charcoals 3 and 7 (Table III) are inverted for the acid series. Whereas in the less activated charcoal the longer chain acids reach equilibrium sooner, in the more activated charcoal the shorter chain acids do so. For the charcoal with smaller pores (Charcoal 3) the time for penetration of the solution is the slow process. Therefore the longer chain acids reach their limiting porosity sooner. For the charcoal with larger pores (Charcoal 7), in which all the acids penetrate to about the same internal area, the rate of diffusion of the acid molecules from the external solution to the adsorbed layer is the slow process. Therefore the shorter chain acids reach equilibrium sooner.

Acknowledgment

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PHOTOMETRIC MICRODETERMINATION OF CALCIUM[1]

By H. A. DeLuca[2]

Abstract

A method is described for the photometric determination of amounts of calcium ranging from 0.04 to 0.16 mgm. The calcium is precipitated as the oxalate. The latter is converted to the carbonate by heating at 475° to 500° C. for one hour. The carbonate is dissolved in 1 ml. of 0.01 *N* hydrochloric acid. The excess acid is allowed to liberate iodine by reacting with potassium iodate and potassium iodide. The absorption of the iodine solution is measured by use of an Evelyn colorimeter, and the calcium originally present in the sample is determined from calibration data.

Introduction

During the course of an investigation involving the estimation of the inorganic constituents of animal tissues, it became necessary to determine small amounts of calcium. The colorimetric method presented here was developed for this purpose.

Sobel and Kaye (5) have described a procedure for the determination of calcium based upon the following reactions.

$$Ca^{++} + C_2O_4^{--} \rightarrow CaC_2O_4 \quad (1)$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \quad (2)$$

$$CaCO_3 + HCl \text{ (excess)} \rightarrow CaCl_2 + H_2O + CO_2 \quad (3)$$

$$6HCl + KIO_3 + 5KI \rightarrow 3I_2 + 3H_2O + 6KCl \quad (4)$$

The calcium is precipitated as the oxalate (Equation 1). The calcium oxalate is converted into the carbonate by heating (Equation 2). A known amount of hydrochloric acid is added to the calcium carbonate (Equation 3). The acid remaining after the carbonate has been neutralized is allowed to liberate iodine (Equation 4). The amount of iodine thus produced is maximal in the absence of calcium in the sample and decreases as the calcium content becomes greater. In the method of Sobel and Kaye this iodine is determined by titration with sodium thiosulphate whereas in the present method the photoelectric colorimeter is utilized for this purpose.

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Method

Reagents

Hydrochloric acid, approximately 0.01 *N*

Hydrochloric acid, approximately 2 *N*

Bromphenol blue, 0.04%, prepared according to the method of Clark (1)

Ammonium oxalate, saturated solution

Ammonium oxalate, 0.5% solution

Ammonium hydroxide, approximately 1 *N*, prepared by diluting 7 ml. of concentrated ammonium hydroxide to 100 ml.

Potassium iodate, 0.5% solution

Potassium iodide, 10% solution

Potassium iodide, 10% solution in 0.002 *N* sodium hydroxide; 10 gm. of potassium iodide and 10 ml. of a stock solution of 0.02 *N* sodium hydroxide are made up to 100 ml.

Calcium solution, 2.00 mgm. of calcium per ml., prepared by dissolving 0.500 gm. of chemically pure calcium carbonate in sufficient 2 *N* hydrochloric acid and diluting with distilled water to 100 ml. Before the final adjustment of volume is made, 1 ml. of concentrated hydrochloric acid is added in order to prevent the growth of moulds.

Procedure

Between 0.04 and 0.16 mgm. of calcium contained in 5 ml. of solution is measured into a selected Pyrex centrifuge tube (see Discussion). One drop of bromphenol blue, sufficient 2 *N* hydrochloric acid to change the colour of the indicator to its acid colour, and 0.2 ml. of saturated ammonium oxalate are added in the order given. The pH is adjusted to approximately 3.5 (a faint blue colour of the indicator) by adding 1 *N* ammonium hydroxide drop by drop.

The tube is allowed to stand for one to two hours with occasional shaking and is then centrifuged for 15 min. at 3000 r.p.m. The supernatant liquid is decanted and the tube inverted on a blotter or towel for 10 min. The mouth of the tube is wiped dry with a small piece of filter paper. The precipitate is then suspended in 0.3 ml. of 0.5% ammonium oxalate and the tube is again centrifuged for 15 min. As before, the supernatant liquid is removed by decantation and the tube inverted for a 10 min. period.

The centrifuge tube is then placed in a cold muffle furnace. The temperature is gradually raised to 475° to 500° C. and held there for at least an hour. The tube is then allowed to cool to room temperature after which exactly 1 ml. of 0.01 *N* hydrochloric acid is added. Solution of the calcium carbonate is facilitated by means of a stirring rod, which is left in the tube during subsequent operations. Heating the tube in a water-bath (85° to 95° C.) for 15 min. with occasional stirring completes solution and expels the carbon dioxide.

The tube is then stoppered with a one-hole rubber stopper, through which the stirring rod is allowed to pass. After cooling for 30 min. to room temperature, 0.2 ml. of 0.5% potassium iodate and 0.2 ml. of 10% potassium iodide are added in that order. The tube is allowed to stand for 15 min. to ensure complete liberation of the iodine, at the end of which time 10 ml. of the alkaline 10% potassium iodide is pipetted into the tube. The contents is then rinsed into a 25 ml. volumetric flask and made up to volume.

Prior to the reading of the solutions in the colorimeter (420 mμ), the latter is adjusted by the following procedure. To 1 ml. of distilled water contained in a centrifuge tube are added 0.2 ml. of 0.5% potassium iodate and 0.2 ml. of 10% potassium iodide. The tube is allowed to stand for 15 min., at the end of which time 10 ml. of the alkaline 10% potassium iodide is added. The contents of the tube is diluted to 25 ml. as before. Two such tubes are prepared and the colorimeter is adjusted to the average of the so-called 'centre-settings'. (The centre-setting is given by the reading of the galvanometer following the removal of the tube as prepared above from the colorimeter, the latter having previously been set to read 100 with this tube in place). The iodine solutions obtained from the samples are now read in the colorimeter and their calcium content is determined from calibration data.

Calibration Curve

Samples containing known amounts of calcium ranging from 0.04 to 0.16 mgm. per 5 ml. in steps of 0.01 mgm. were prepared from the stock solution. For the purpose of ascertaining what precision could be expected from the method, four samples of each concentration were treated according to the procedure given above. The results are given in Table I and are shown

TABLE I

CALIBRATION DATA

(1) Calcium, mgm.	(2) Galvanometer readings	(3) Slope of curve, mgm. per division	Mean deviation		Range of values Max. → Min.	
			(4) Of galvanometer readings	(5) Of calcium, as %	(6) Of galvanometer readings	(7) Of calcium, as %
0.00	17.9	—	±0.0	—	—	—
0.04	24.0	0.0067	±0.1	±1.7	0.2	3.4
0.05	26.2	0.0045	±0.1	±0.9	0.4	3.6
0.06	27.4	0.0040	±0.4	±2.7	0.9	6.0
0.07	31.4	0.0036	±0.2	±1.0	0.6	3.1
0.08	33.8	0.0031	±0.3	±1.2	1.1	4.3
0.09	37.0	0.0025	±0.8	±2.2	2.0	5.6
0.10	40.8	0.0024	±0.7	±1.7	1.8	4.3
0.11	45.8	0.0022	±0.3	±0.6	0.9	1.8
0.12	51.9	0.0019	±0.5	±0.8	1.4	2.2
0.13	55.2	0.0017	±0.4	±0.5	1.2	1.6
0.14	62.4	0.0015	±1.1	±1.2	3.6	3.9
0.15	70.8	0.0013	±1.3	±1.1	3.1	2.7
0.16	78.5	0.0010	±0.5	±0.3	1.0	0.6

graphically in Fig. 1. The mean value and deviation for the galvanometer readings are shown in Columns 2 and 4, respectively. By using the slope of the curve at each point (Column 3), the mean deviation of the galvanometer readings has been calculated as a percentage of the amount of calcium present

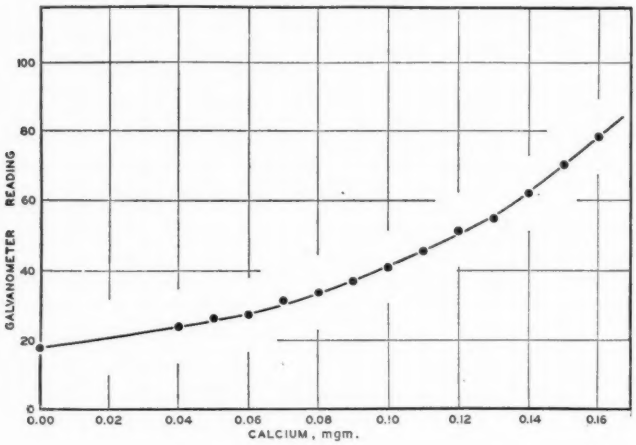

Fig. 1

(Column 5). In Column 6 is given the difference between the minimum and maximum values of the galvanometer readings for the four samples at each concentration. In Column 7 this difference is expressed as a percentage of the calcium present.

Sixty-two determinations were performed during the course of the calibration. The results from six of these were discarded, as the deviations from the mean in these instances were of a magnitude suggestive of manipulative error.

Discussion

The Pyrex centrifuge tubes used for the determinations were selected with some care. Only those with the most constricted tips were chosen, as such tubes appeared to hold the precipitate more firmly during decantation of the supernatant liquid.

The use of 5-ml. samples for the calcium precipitation was adopted for several reasons. Some of the tissue solutions to be analysed were so dilute that a smaller volume did not contain an amount of calcium sufficient for analysis by the colorimetric method. On the other hand, more concentrated solutions could be analysed by selecting a suitable volume and diluting it to 5 ml. with distilled water prior to the precipitation of the calcium. The use of a larger volume has the additional advantages that it simplifies the adjustment of the pH to a given value, and that during decantation there is a more complete recovery of the supernatant liquid, which is desirable when further analysis is contemplated.

A somewhat lower temperature for the conversion of calcium oxalate to the carbonate has been employed inasmuch as heating at 560° C. for one hour, as recommended by Sobel and Kaye, resulted in samples that had almost no ability to neutralize the acid solution. Siwe (4) has indicated that unless special tubes are used, the calcium precipitate may attack the glass at temperatures of 550° to 600° C. Data obtained by Willard and Boldyreff (6) show that the oxalate–carbonate conversion proceeds to completion in one hour at a temperature of 450° C.

The potassium iodide solution decomposes with time to yield free iodine. Decomposition proceeded slowly in the stock solution contained in a brown glass bottle, but the same solution decomposed more rapidly after transference to a smaller clear glass container. The potassium iodate solution appeared quite stable. Sobel and Kaye (5) give a simple procedure for testing both reagents at once, namely, the mixing of equal volumes of the iodide and iodate solutions followed by the addition of a few drops of a starch solution. Actually, a small amount of free iodine should be of no consequence in a colorimetric method inasmuch as the use of a blank corrects for this. Notwithstanding, fresh solutions were prepared whenever decomposition of the iodide had occurred.

The alkaline 10% potassium iodide solution is used for a twofold purpose. First, it prevents the evaporation of the iodine liberated, and second, it acts to intensify the colour of the latter. Both of these effects are produced by the formation of the compound KI_3, as pointed out by Sendroy and Alving (3). Decomposition of the potassium iodide is overcome by the use of the sodium hydroxide, as suggested by Flox, Pitesky, and Alving (2). This is especially desirable at this point of the procedure owing to the fact that such a large volume (10 cc.) of the iodide solution is necessary to achieve the purposes indicated above. However, experiment indicates that this solution should not be much more alkaline in the sodium hydroxide than 0.002 *N*. Solutions of higher concentration (0.01 *N*) caused a disappearance of a detectable amount of the iodine liberated in the course of the calcium analysis, probably as a result of the reaction given below.

$$2NaOH + I_2 \rightarrow NaI + NaIO + H_2O$$

The exact normality of the 0.01 *N* hydrochloric acid need not be known. It is advisable to prepare a reasonably large volume of this acid at one time in order to avoid the necessity of recalibrating the colorimeter with each fresh batch of this reagent. Hydrochloric acid of this concentration was found to be quite stable. The iodine liberated by 1 ml. of acid (which is the equivalent of an analysed sample containing no calcium) as measured in the colorimeter may be used to indicate any change in the strength of the acid. In measuring the latter, the same pipette was used throughout the calibration and subsequent analyses.

Several departures from the customary use of the Evelyn colorimeter were made. A single colorimeter tube was used in obtaining the calibration curve and in all analyses. After reading a solution in the colorimeter, the contents was poured from the tube, and the tube allowed to drain for a few seconds. The tube was then rinsed with several 3 ml. portions of the solution about to be measured. Inasmuch as this avoids the differences in colorimeter tubes, it is thought justifiable to report the galvanometer readings to the nearest 1/10 division rather than to the nearest $\frac{1}{4}$ division, as suggested in the directions accompanying the instrument.

A consideration of the results obtained for the calibration curve indicates what precision may be expected in the analysis of samples of unknown calcium content. For the lowest amount of calcium (0.04 mgm.) the galvanometer readings for the four samples (23.8, 24.0, 24.0, 24.0) show smaller differences, but the percentage error is relatively large. A glance at Table I shows that at this point a difference of 0.1 division in two galvanometer readings produces a deviation of nearly 2%. For samples containing larger amounts of calcium (0.15 mgm.), the galvanometer readings (69.2, 69.8, 72.0, 72.3) show much larger differences, but these cause relatively smaller percentage deviations.

The method as described above cannot be used for samples containing more than 0.16 mgm. calcium. However, it could be extended readily to higher values simply by employing greater volumes or stronger solutions of the reagents indicated.

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COAGULATION AND SURFACE LOSSES IN DISPERSE SYSTEMS IN STILL AND TURBULENT AIR[1]

By G. O. Langstroth[2] and T. Gillespie[3]

Abstract

Smoke chamber studies have been made of the ageing of ammonium chloride smokes under various controlled degrees of turbulent air motion as well as in still air. The changes in mass concentration and particle number were followed for 5.5 hr. under each set of conditions, and some data on particle size distribution were obtained. The logarithm of the mass concentration was found to vary linearly with time under all conditions. None of the particle number data lent themselves to interpretation on the basis adopted by previous workers. They were described quantitatively by equations developed from general postulates which take into account loss to various surfaces. The equations permitted analytical separation of coagulation and surface effects, and the constant descriptive of the latter was closely related to that associated with mass loss. The coagulation constant for still air was found to be only slightly greater than the ideal Smoluchowski value. A description was obtained of the manner in which the various constants increased with the degree of air motion.

The ageing of aerosols in still air has been studied extensively (for general discussions, see references 13 and 14).* It has been found (6, 9, 10, 14*) that the increase in particulate volume ($1/n$) with time (t) may be represented by

$$1/n = 1/n_0 + Kt, \tag{1}$$

where n denotes the number of particles per cubic centimetre at time t, and n_0 that at an early arbitrary time origin. Data given in the literature do not extend beyond ageing times of about 100 min. but it has been stated (9) that the linear relation holds for intervals as long as 250 min. It has been customary to interpret K as the coagulation constant. The values determined for it have been considerably greater than that for an ideal aerosol as calculated from a modification of Smoluchowski's theory of coagulating sols (2, 8, 9, 14).

The ageing of aerosols in turbulent air has received comparatively little attention. The results of studies that have been made (4, 11) do not lend themselves readily to interpretation in terms of fundamental processes because of the difficulty of translating the Tyndall beam brightness data obtained to terms of particle number and size. Except in specially designed laboratory experiments, however, problems involving turbulent air conditions are most often encountered.

In the attempt to obtain a better understanding of the factors involved in the general ageing process, studies have been made of ammonium chloride smokes under various controlled degrees of turbulent air motion ranging from the static condition upward. The changes in the mass of dispersed material and number of particles per cubic centimetre (mass concentration and particle

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* *And "Disperse systems in gases", in Trans. Faraday Soc., Vol. 32, pp. 1042-1300. 1936.*

number) were followed for 330 min. under each set of conditions. None of the data for these long periods, including data for still air, could be interpreted on the basis that coagulation was the sole factor responsible for the reduction in particle number. They are described, however, by equations developed from general postulates. The equations permit an analytical separation of effects produced by coagulation and by loss to adjacent surfaces, and are consistent with fact in the various points for which a comparison has been possible. Changes in the degree of air motion alter the values of constants in the equations so that the effect on the processes involved may be described with the aid of determined curves for the constants. In particular, the relation between particulate volume and time differs in form from that given in Equation (1).

1. Apparatus, Techniques, and Experimental Procedure

(*a*) *The Smoke Chamber and Stirring Mechanism*

The smoke chamber was a 1.12 m. cube having its internal walls finished with acid-proof paint. The stirrer used to produce air motion consisted of two 60.5 by 32.5 cm.^{2} coplanar cardboard vanes mounted at the ends of a 60.5 by 91.5 cm.^{2} light wooden frame so that a gap of 26.5 cm. was left between them. Each vane was pierced by a series of 15 equally spaced 5 by 5 cm.^{2} holes. The stirrer was supported on a horizontal axle parallel to the length of the vanes and passing down the middle of the central gap. It was oscillated through an angle of 180° from the vertical at any selected frequency by a motor driven system of gears and shafts external to the chamber. The frequency was determined with the aid of a revolution counter incorporated in the driving system. This device was used in preference to ordinary fans because of its periodic reversal of motion, the ease of control and adjustment, and its well defined characteristics as a stirrer.

(*b*) *Specification of the Degree of Air Motion*

The average amount of air passing through a given small volume per unit time regardless of direction was taken as an index of the degree of air motion. The characteristics of the air motion with different stirring rates were investigated with the aid of an instrument of the heated thermocouple type developed for the purpose. The head of the device consisted of six thermocouple junctions with heating coils, arranged in the form of a child's jack and extending about 1.5 cm. in each dimension. The readings were independent of the direction of air flow, and the time lag was not excessive (equilibrium was attained within one minute on an abrupt change from 12 to 46 m. per min. steady air velocity). The instrument was calibrated under conditions of uniform air flow. Readings of the effective air speed for different stirring rates were made at 16 systematically distributed points throughout the chamber in a series of preliminary experiments. They were found to be closely proportional to the oscillation frequency of the stirrer. Furthermore, they were remarkably similar at different points, excepting those close within

the corners of the chamber. For example, with a frequency of 30 min.$^{-1}$, they varied only from 34 m. per min. for points directly off the high velocity outer edge of the stirrer to 29 m. per min. for points near the wall at the axle; with the device mounted on the stirrer the reading was 40 m. per min., but it decreased to 17 m. per min. close within the corners. In presenting the results on smoke a value V (m. per min.) has been assigned to each experiment as an index of the degree of air motion. This value is the space-average air speed (as found in preliminary experiments) corresponding to the stirrer oscillation frequency used.

(*c*) *Production of the Aerosol*

The smoke generator consisted of a centrifugal blower whose output passed through a control valve into a 7 cm. diameter metal pipe leading into the chamber. The pipe contained a Pitot tube to permit adjustment of the air flow to a standard value, and a nichrome heating coil placed near the exit end. A standard amount (87 mgm.) of ammonium chloride placed in a Pyrex boat on the coil was decomposed in two minutes with a heating current of 8.0 amp. A small fan within the chamber provided rapid cooling and dilution of the products as they emerged from the exit end of the pipe. The generator was designed with the aim of obtaining a series of aerosols of similar characteristics, for it is known (10, 14) that reproducibility is favoured with 'blown' smokes. In our experiments the mass concentration at three minutes after completion of smoke production varied from about 40 to about 60 mgm. per m.^{3} and the corresponding particle number from about 2×10^5 to about 4×10^5 cc.$^{-1}$ (Table III).

(*d*) *Determination of Mass Concentration*

Samples were obtained by electrical precipitation using a modified form of the tube (diameter 1.2 cm., length 6.5 cm.) described by Drinker and Hatch (3). The central electrode was enclosed in Pyrex to permit thorough cleaning and to avoid contamination. In sampling, 500 cc. of the aerosol was first drawn through the precipitator with no applied voltage by lowering the water level in an attached system. A further volume of 250 to 4000 cc. (depending on conditions) was then drawn through with an applied voltage of 10 kv., which produced a discernible glow between the electrodes. The deposit was dissolved in 50 cc. of distilled water, and the resulting solution was analysed with Nessler's reagent. Precipitates ranged from 0.040 to 0.002 mgm. of ammonium chloride. Tests carried out with two precipitator tubes in series indicated that precipitation was complete for aerosols both in the early and late stages of life. The initial flushing procedure, which was required to obtain a sample representative of the aerosol in the chamber, did not result in a detectable deposit in the precipitator tube.

(*e*) *Determination of Particle Number*

A thermal precipitator (7)* mounted on a 2.5 cm. diameter brass tube extending 10 cm. into the chamber was used in the determination of the number

* *See also "Disperse systems in gases", in Trans. Faraday Soc., Vol. 32, pp. 1042-1300, 1936.*

of particles per cubic centimetre. In taking a sample, 500 cc. of the aerosol was first drawn through the brass tube from an exit at the precipitator end, and 5 cc. was drawn through the cold precipitator by lowering the water level in an attached small-bore graduated tube. A current of 1.25 amp. was then passed through the precipitator wire (No. 32 B & S nichrome) and a volume of 0.5 to 10 cc. (depending on conditions) was drawn through, starting 5 to 10 sec. after the current had been turned on. The flow rate of 2 to 4 cc. per min. was well below the value of 6.5 cc. per min. suggested (7) as an upper limit for efficient deposition, and the deposits formed on the polished glass disks had straight, sharp, leading edges—a characteristic indicative of complete precipitation (7). The deposit formed during the initial flushing procedure was found to be negligible. It was necessary to stop the stirring mechanism during sampling: the stoppage period was not more than one minute for each sample.

The deposits on the disks were 9 mm. long and less than 1 mm. wide. They were examined under a magnification of 440 × using dark field illumination produced by a narrow light beam approximately normal to the optic axis of the microscope. The number of particles in each of 10 equally spaced crosswise strips of width 2.3×10^{-3} cm. was counted for each deposit with the aid of a mechanical stage and a Whipple disk in the eyepiece. The known ratio of the examined to the total area of the deposits permitted calculation of the total number of particles deposited, and the number of particles per cubic centimetre was found from this value and the known volume of the sample. The fact that samples taken with no smoke in the chamber gave inappreciable counts ruled out dust as a complicating factor in these experiments.

In some of the earlier experiments, aerosol samples were diluted with air before precipitation in order to reduce the particle number and thus facilitate counting. The validity of the procedure was established by comparing the results for a series of direct and diluted samples taken alternately. Dilution was abandoned on arranging to draw samples of 0.5 to 1.0 cc. with an accuracy of 3%.

(f) Particle Size Estimation

Four subsidiary experiments, two with still air and two with a high degree of air motion (V = 50 m. per min.) were performed to provide information on particle size distribution. Thermal precipitator samples were taken every 30 min. for a period of 280 min. The deposits were examined with substage illumination and a magnification of 950 ×. The particles in crosswise strips selected as for particle number counts were classified into size groups by comparing them with the smallest square in the Whipple disk (projected area 2.2×2.2 μ). Since this procedure is based on the appearance in two dimensions it may be subject to systematic error. The size groups adopted

were: less than 0.3, 0.3 – 0.6, 0.6 – 0.9, 0.9 – 1.1, 1.1 – 1.4, 1.4 – 1.7, and 1.7 – 2.2 μ in apparent radius. In the results shown in Fig. 3, the number in each size group expressed as a percentage of the total has been plotted at the median radius for the group, that for the first being plotted at 0.2 μ.

(*g*) *The Procedure in Ageing Studies*

The generation of smoke was complete within a two minute period but the fan in the chamber was operated for three minutes longer. It was then turned off and the stirrer set in oscillation and maintained at the selected oscillation frequency. All subsequent times were reckoned from a zero set at the moment of turning off the fan. Particle number and mass concentration samples were taken at intervals of 30 min. for a period of 5.5 hr. (see Tables I and I*A*). Counts were made for the former immediately, but analysis of the latter was permissible at any period within 24 hr. if the precipitation tubes were well stoppered. The total volume drawn from the chamber during an experiment in flushing and sampling did not exceed 1.7% of the chamber volume. A series of experiments was performed with various degrees of air motion (see Tables I and I*A*). After each the chamber was well aired and cleaned.

The deposit on the bottom of the chamber at the end of an experiment under still air conditions was visibly greater than the deposit on the top and side walls. With stirred air, the distribution of the deposit appeared similar although the stirrer acquired a deposit similar to that on the bottom of the chamber.

A series of experiments was performed to ascertain the extent to which particles deposited on the walls were swept off again by air motion. The procedure was identical with that already described, but all surfaces were coated heavily with oil. Since subsidiary tests showed that particles were wet immediately on striking an oiled surface, it seems reasonable to assume that return to the aerosol was eliminated in these experiments.

2. Experimental Data

Particulate volume ($1/n$) and mass concentration (m) data for a series of experiments (serial numbers *D*38, *D*40, etc.) are given respectively in Tables I and I*A*. The corresponding data obtained with oiled chamber walls are given in Tables II and II*A*. For reasons to appear later, values calculated from Equation (7) are included in Tables I and II. It appears desirable that the data be given in some detail since the interpretation differs fundamentally from that given previously by various workers for data covering a more restricted range.

TABLE I

PARTICULATE VOLUME VS. TIME DATA (DRY CHAMBER WALLS)

The tabulated values are $10^6/n$ cc.*

t, min.	V = 0 m./min.				V = 1.1 m./min.		V = 5.4 m./min.	
	*D*38		*D*40		*D*75		*D*74	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	5.2	5.6	4.8	5.2	—	—	—	—
2	—	—	—	—	—	—	—	—
5	—	—	—	—	2.7	3.6	2.1	2.9
30	6.8	6.8	7.1	6.6	4.3	4.7	3.6	4.0
60	8.3	8.2	7.6	7.9	6.7	6.0	5.8	5.8
90	10.4	9.5	9.5	9.5	8.6	7.6	7.3	7.7
120	—	—	11.4	11.2	9.7	9.4	10.1	10.0
150	—	—	—	—	10.7	11.3	11.8	12.9
180	14.0	14.6	15.2	15.1	11.9	13.8	15.7	16.1
210	15.8	16.7	17.4	17.7	15.5	17.2	21	20
240	19	19	21	20	19	19	25	25
270	22	21	24	23	20	23	29	30
300	24	24	28	26	28	27	36	36
330	26	27	29	30	32	31	43	44

t, min.	V = 11 m./min.				V = 22 m./min.		V = 29 m./min.			
	*D*76		*D*77		*D*73		*D*56		*D*58	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	—	4.8	4.5	—	—
5	3.5	3.5	4.3	4.4	4.3	4.8	—	—	3.1	3.3
30	4.9	4.8	6.3	5.8	6.0	6.3	5.4	6.2	5.4	4.7
60	6.5	6.6	8.2	8.6	9.5	8.8	10.8	8.5	7.5	7.7
90	8.6	8.9	9.0	9.8	12.1	11.4	13.2	11.2	8.4	9.1
120	11.2	11.5	11.1	12.3	14.3	14.8	—	—	12.7	12.3
150	14.6	15.0	14.0	15.2	19	19	17.4	18.2	16.0	15.8
180	22	19	20	19	26	24	24	23	21	20
210	25	24	22	23	31	29	29	29	27	26
240	30	30	27	28	35	36	35	35	31	33
270	33	37	34	34	41	44	47	44	45	41
300	46	46	43	42	59	54	54	54	52	52
320	57	53	—	—	—	—	—	—	—	—
325	—	—	—	—	—	—	—	—	61	62
330	—	—	54	50	67	66	62	66	—	—

**Values under the heading 'Calc' were calculated from Equation (7) with the constants as given in Table III.*

PARTICULATE VOLUME VS. TIME DATA (DRY CHAMBER WALLS)—*Continued*
The tabulated values are $10^6/n$ cc.*—*Continued*

t, min.	*V* = 35 m./min.				*V* = 40 m./min.				*V* = 50 m./min			
	*D*62		*D*63		*D*54		*D*55		*D*51		*D*60	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	—	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	7.3	5.8	5.6	4.8	4.4	4.0	—	—
5	3.3	3.3	—	—	—	—	—	—	—	—	—	—
30	5.4	5.0	6.0	6.5	—	—	9.0	7.3	6.5	7.0	6.0	7.2
60	6.8	7.5	9.9	9.5	8.2	11.4	8.5	11.0	12.9	11.5	12.8	11.5
90	12.6	11.0	15.9	13.5	16.7	16.3	12.8	15.8	16.3	17.4	23	18
120	15.2	15.0	—	—	22	22	26	22	28	25	26	25
150	19	20	23	24	28	29	30	30	38	36	29	35
180	27	27	32	31	54	39	43	40	53	50	43	49
210	34	36	43	41	53	51	55	53	73	70	69	69
240	46	48	52	52	64	67	68	70	98	96	97	95
270	65	63	61	67	88	89	92	93	128	129	—	—
300	82	82	79	85	115	113	125	123	176	176	164	176
320	—	—	—	—	—	—	—	—	—	—	—	—
325	—	—	—	—	—	—	—	—	—	—	250	233
330	109	107	118	109	145	145	147	159	232	239	—	—

**Values under the heading 'Calc.' were calculated from Equation (7) with the constants as given in Table III.*

TABLE IA

MASS CONCENTRATION (MGM. PER M.^{3}) VS. TIME DATA FOR THE EXPERIMENTS OF TABLE I

t, min.	*V* = 0		1.1	5.4	11		22
	*D*38	*D*40	*D*75	*D*74	*D*76	*D*77	*D*73
10	38	46	44	40	44	44	44
40	38	44	38	33	33	—	33
70	32	38	35	26	23	25	25
100	26	34	27	20	19	20	17
130	24	37	30	18	15	15	12.5
160	20	32	18	15	14	13	12.0
190	18	25	17	12.5	10	10	8.0
220	23	20	14	10	6.7	7	5.2
250	19	25	13	10	5	6.7	6.0
280	17	21	13	8	4	5	3.3
310	14.6	20	—	—	—	—	—

t, min.	*V* = 29		35		40		50	
	*D*56	*D*58	*D*62	*D*63	*D*54	*D*55	*D*51	*D*60
10	42	52	40	48	47	53	43	44
40	33	40	33	37	37	40	27	23
70	30	35	25	27	22	23	23	20
100	20	25	16	14	16	15	12	12
130	14	22	12	11	12	12	6	11
160	18	18	10.6	10.5	12	10	8	6.5
190	12	13	8	9	7.5	7	4	5.3
220	8.7	6.5	5.5	5.5	5	3	3	3
250	5	6.0	4	4	3.5	3.5	1.3	1.5
280	4	—	5	4	2.8	2.7	0.8	1.2
310	—	—	—	—	—	—	—	—

TABLE II

DATA CORRESPONDING TO TABLE I BUT FOR OILED CHAMBER WALLS

t, min.	$V = 0$		$V = 11$				$V = 40$	
	*W*80		*W*78		*W*79		*W*81	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
5	2.4	3.0	2.5	2.9	2.9	3.0	2.5	2.6
30	4.3	4.1	4.1	4.1	4.1	4.0	4.5	4.5
60	5.6	5.3	5.9	5.6	6.7	5.5	7.7	7.2
90	7.1	6.7	7.5	7.3	7.9	7.3	10.5	10.7
120	8.0	8.0	9.8	9.7	9.0	9.3	13.3	15.1
150	9.7	9.6	11.1	12.0	11.8	11.9	20	21
180	11.3	11.1	14.2	15.0	15.7	14.8	28	29
210	12.9	13.2	19	19	18.3	18.0	39	39
240	16.5	15.3	22	23	23	22	48	51
270	16.8	17.7	27	28	25	27	63	67
300	20	20	32	34	33	33	90	88
330	26	23	41	41	—	—	—	—

TABLE IIA

MASS CONCENTRATION (MGM. PER M.^{3}) VS. TIME DATA FOR THE EXPERIMENTS OF TABLE II

t, min.	$V = 0$	11		40
	*W*80	*W*78	*W*79	*W*81
10	40	44	44	42
40	34	30	31	23
70	28	28	28	15
100	27	22	23	14
130	24	18	19	10
160	25	16	18	9
190	21	13	15	6
220	18	10	11	3.3
250	18	9.0	10	2.5
280	17	8.0	9.0	—

Particulate volume vs. time plots in the manner of previous workers are shown in Fig. 1 for some of the data. They are not described by Equation (1). Even for still air the curve exhibits a concavity upward, although for a period of about 200 min. it is reasonably linear. The initial portion has a slope corresponding to a K value of 5.1×10^{-8} cc. per min. as defined by Equation (1), compared to values ranging from 3.0×10^{-8} to 7.9×10^{-8} cc. per min. obtained for ammonium chloride smoke by previous workers (6; 9; 10; 14, p. 46).

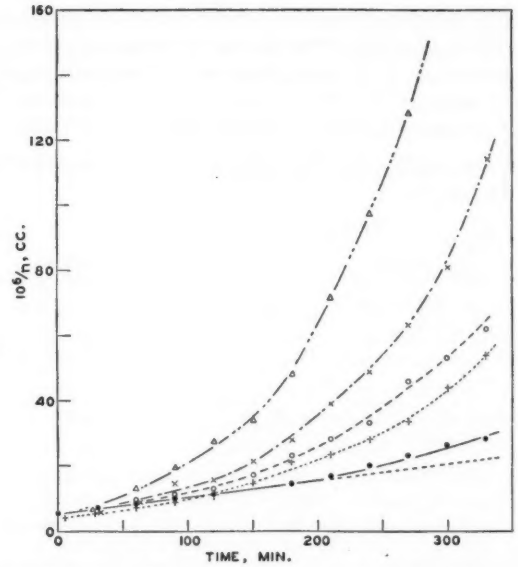

FIG. 1. *Particulate volume vs. time curves for various degrees of air motion. The symbols* ●, +, ○, ×, *and* △ *are associated respectively with V values of 0, 11, 29, 35, and 50 m. per min. Each point is an average value for two experiments.*

Plots of log (m) vs. time as illustrated in Fig. 2 were found to be linear for all degrees of air motion over the investigated range. This relation has been reported previously (12) to hold for various types of fanned smokes. In addition, some still air data from the literature, when plotted similarly, provide further support. Not only are the plots linear but their slopes are strikingly similar. For example, the data for two zinc oxide smokes studied

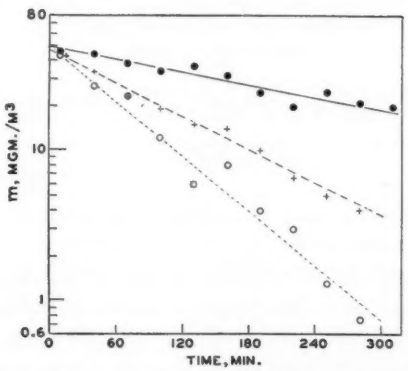

FIG. 2. *Mass concentration vs. time curves for various degrees of air motion. The symbols* ●, +, *and* ○ *are associated with V values of 0, 11, and 50 m. per min. The points represent single determinations.*

by Whytlaw-Gray and Speakman (15) yield a 'mass loss constant' (defined by Equation 3) of 3.6×10^{-3} min.$^{-1}$ on disregarding the first point in each which is stated to be erroneous, while some data for an ammonium chloride smoke (14, p. 19) give a value of 3.0×10^{-3} min.$^{-1}$. In comparison, our own data for still air yield values of from 3.2×10^{-3} to 3.6×10^{-3} min.$^{-1}$ (Table III).

The results of the particle size distribution experiments described in Section 1 (*f*) are given in Fig. 3.

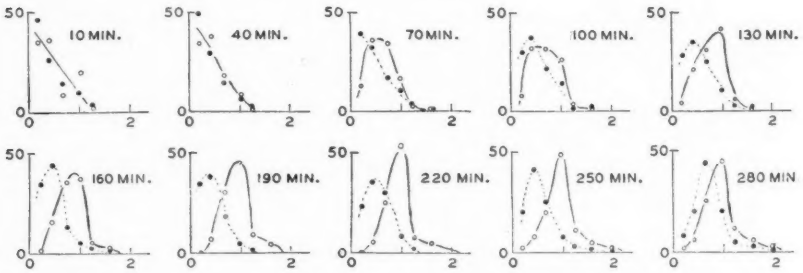

FIG. 3. *Estimated particle size distributions. The symbols ○ and ● are associated with V values of 0 and 50 m. per min. The ordinates refer to the frequency and the abscissae to the apparent radius in microns.*

3. Theoretical Aspects of the Ageing Process

The following considerations lead to a quantitative description of the experimental data.

In a turbulent medium, air is being brought constantly into contact with various surfaces, and since practically all particles striking a surface stick to it (Ref. 5, and the present data) there is a consequent decrease in mass concentration and particle number. The rate of decrease in the former quantity under a given set of conditions should be proportional to the mass concentration m, so that

$$dm/dt = -\alpha m , \tag{2}$$

where α denotes the 'mass loss constant'. It follows that

$$\ln(m) = \ln(m_0) - \alpha t \tag{3}$$

over periods for which α may be taken as independent of time, where m_0 denotes the mass concentration at $t = 0$. As previously stated, Equation (3) describes our data and receives strong support from other sources.

Other things being equal, the chance of a particle striking a surface should be proportional to the particle number n, so that the rate of decrease in particle number due to such loss is

$$(dn/dt)_l = -\beta n , \tag{4}$$

where β denotes the 'loss constant'. Since the chance of collision between two particles is proportional to n^2, the rate of decrease in particle number because of coagulation may be written,

$$(dn/dt)_c = - kn^2, \tag{5}$$

where k denotes the coagulation constant. It follows that the total rate of decrease in n is

$$dn/dt = - (kn^2 + \beta n) . \tag{6}$$

Both k and β may be expected to increase with increasing air motion because of the greater chance of particle collisions and of the increased rate at which air is brought into contact with surfaces. For aerosols confined in a chamber, β should depend on chamber geometry since a large ratio of wall surface to volume must favour rapid removal of particles. In addition, both k and β may be expected to depend to some extent on particle size, i.e., the greater mobility of small particles favours a high collision rate and the greater momentum of large particles a high loss rate on deflection of air currents at surfaces. Particle size is subject to change during the ageing of an aerosol, and strictly speaking k and β are functions of time.

For intervals over which time variations in k and β may be disregarded, it follows from Equation (6) that

$$\ln(1/n + k/\beta) = \ln(1/n_0 + k/\beta) + \beta t , \tag{7}$$

where n_0 denotes the particle number at $t = 0$. Furthermore,

$$n = n_0 e^{-\beta t}/\phi \tag{8}$$

$$(\Delta n)_t = \beta/k . \ln \phi , \tag{9}$$

where $\phi = 1 + n_0 k/\beta . (1 - e^{-\beta t})$ and $(\Delta n)_t$ denotes the reduction in particle number due to surface losses during the interval 0 to t. The corresponding expression for coagulation losses is readily found.

A close relation may be expected to exist between the loss constant β and the mass loss constant α. If the average mass of particles in the aerosol and of those lost to surfaces at a given time be denoted by μ and μ', respectively, one may write $m = \mu n$ and $dm/dt = \mu'(dn/dt)_t$. Hence in view of Equations (2) and (4),

$$\alpha/\beta = \mu'/\mu . \tag{10}$$

For an ideal homogeneous smoke α and β should be equal.

Previous workers have adopted Equation (1) of the introduction in the interpretation of ageing data for still air. This relation follows directly from integration of Equation (5) with K substituted for k, i.e., constancy of mass concentration is assumed. The mechanisms responsible for the observed decrease in mass concentration in still air may involve sedimentation, diffusion

of particles to surfaces, and air currents set up by temperature gradients and disturbances caused in sampling. Whatever their nature it appears reasonable to assume that the rate of decrease in particle number and in mass concentration due to surface losses are proportional to n and m, respectively, as specified by Equations (4) and (2). On this basis Equations (2) to (10) should be applicable to still as well as to turbulent air conditions. This expectation is borne out by the experimental data.

It might be thought at first sight that the mechanisms of loss in still and turbulent air have little in common, since in general sedimentation velocity is negligibly small compared to the air velocity in turbulence. The former is, however, always superimposed on the latter, and the time average of the latter is zero. Consequently a tendency for material to be deposited most densely on the surface below the aerosol must be expected, and is found in experiments.

No applicable theory of sedimentation appears to have been worked out in detail. An idea of the importance of diffusion as a loss mechanism in still air is readily obtained from a consideration of the diffusion of homogeneous non-coagulating particles to the 'absorbing' walls of a spherical chamber of radius ρ_0 in the absence of gravity. Analogous equations in the theory of heat flow are well known (1). For a uniform initial distribution, the fraction F of the particles that remains after a time t is given by

$$F = \frac{6}{\pi^2} \sum_l \frac{1}{l^2} e^{-\frac{D\pi^2 l^2 t}{\rho_0^2}}, \tag{11}$$

where l takes on successive integer values, and the diffusion constant D for spherical particles of r microns radius is given (2, 14) by

$$D = 10^4 RT/6\pi N\eta r . \tag{12}$$

R, T, N, and η denote, respectively, the gas constant, the temperature, Avogadro's number, and the coefficient of viscosity of air. According to these equations the loss by diffusion in a five hour period is less than 5% for particles of 0.5 μ radius, and no greater than 10% for particles as small as 0.001 μ in radius. Loss by diffusion therefore seems likely to play only a minor role in the ageing process under laboratory conditions.

The value of the coagulation constant k at room temperature and atmospheric pressure for an ideal aerosol whose spherical particles of r microns radius coagulate on touching may be calculated from the well known expression based on Smoluchowski's theory of coagulating sols (2, 8, 9, 14), i.e.,

$$k = 1.77 \times 10^{-8} (1 + 0.089/r) \text{ cc. per min.} \tag{13}$$

The equation predicts a decrease in k of about 9% when the particle radius increases from 0.5 to 1.0 μ. This feature is of interest in connection with the neglect of the time dependence of k in the integration leading to Equation (7) (cf. Fig. 3).

4. Analysis of the Particle Number Data

Following the suggestion of Equation (7), it was found that plots of log $(10^6/n + E)$ vs. time became linear on selection of a suitable value for the constant E by trial. Examples are shown in Figs. 4 and 5. The linearity of the curve was a fair criterion of the suitability of E for data associated with large V values, but was less critical for plots of smaller slope. Under the worst conditions (still air data) a value of 6 or 7 produced linearity (Fig. 5), but higher values did not result in a noticeable concavity upward such as shown in Fig. 4. In these circumstances a value of E was selected to produce

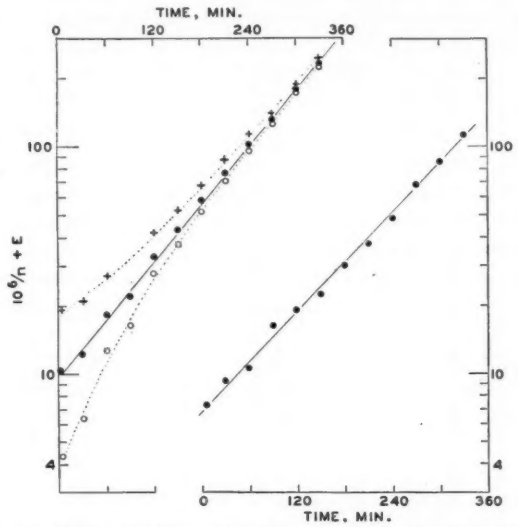

FIG. 4. *Data for single experiments plotted as suggested by Equation (7). The symbols* ○, ●, *and* + *in the plot at the left (abscissae values at the top) are associated with E values of 0, 6.0, and 15, and a V value of 50 m. per min. The plot at the right (abscissae values at the bottom) is associated with an E value of 4.0 and a V value of 35 m. per min.*

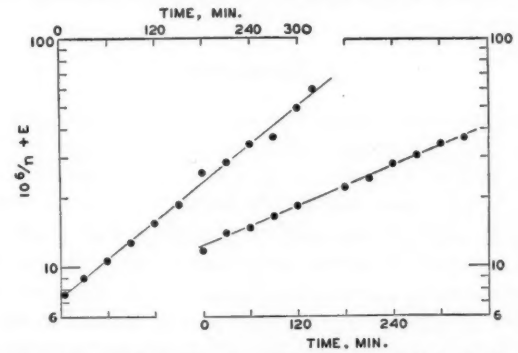

FIG. 5. *A companion graph to Fig. 4. The left and right hand plots are associated respectively with V values of 11 and 0 m. per min., and E values of 4.0 and 7.0.*

linearity and to be consistent with other features to appear later. The loss constant β was calculated from the slopes of the curves, and the coagulation constant k from the values of E and β (see Equation 7). The values of the constants for the entire data are given in Table III.

TABLE III

A SUMMARY OF THE EXPERIMENTAL VALUES OF THE CONSTANTS IN EQUATIONS (3) AND (7)

V, m./min.	Exp. No.	m_0, mgm./m^3	$n_0 \times 10^{-4}$, cc.$^{-1}$	$\alpha \times 10^3$, min.$^{-1}$	$\beta \times 10^3$, min.$^{-1}$	$k \times 10^8$, cc./min.	$k/\beta \times 10^6$	α/β
0.0	*D*38	39	18	3.2	3.0	2.1	7.0	1.1
0.0	*D*40	49	19	3.4	3.3	2.3	7.0	1.0$_4$
0.0	*W*80[1]	41	33	3.6	3.3	2.3	7.0	1.1
1.1	*D*75	47	29	5.2	4.4	2.2	5.0	1.2
5.4	*D*74	43	40	6.2	5.5	2.8	5.0	1.1
11	*D*76	45	31	8.3	6.4	2.6	4.0	1.3
11	*D*77	47	24	7.4	5.8	2.3	4.0	1.3
11	*W*78[1]	45	36	6.8	5.8	2.3	4.0	1.2
11	*W*79[1]	45	34	6.2	5.5	2.2	4.0	1.1
22	*D*73	48	23	9.0	6.2	3.1	5.0	1.4
29	*D*56	47	23	8.1	6.4	3.2	5.0	1.3
29	*D*58	60	32	8.5	6.9	2.8	4.0	1.2
35	*D*62	48	33	9.6	8.3	3.3	4.0	1.2
35	*D*63	48	24	9.6	7.6	3.8	5.0	1.3
40	*D*54	52	18	10.8	9.0	3.6	4.0	1.2
40	*D*55	56	22	11.0	8.7	4.3	5.0	1.3
40	*W*81[1]	40	42	10.8	8.5	4.3	5.0	1.3
50	*D*51	49	26	14.0	9.7	5.8	6.0	1.4
50	*D*60	47	25	12.8	9.9	4.9	5.0	1.3

m_0 and n_0 were obtained by extrapolation of the appropriate time curves.
[1] *Oiled chamber walls.*

5. Discussion

Plots such as Figs. 4 and 5 may give an erroneous impression of the experimental scatter, since a constant has been added to each $10^6/n$ value. For this reason particulate volumes as calculated from Equation (7) using the data of Table III have been included in Tables I and II for comparison with observation. The average deviation of calculated from observed values for the more than 200 determinations given was 6.2%. This is comparable to the scatter of determined points about linear $1/n$ vs. time curves obtained by previous workers for still air and ageing times of about 100 min. Published data (6, 9, 10) exhibit average deviations of about 5, 4, and 7%, and the overall frequency distribution of deviations is almost identical with our own. It

is considered therefore that Equation (7) describes the entire particle number data as well as may be expected in view of the difficulty of attaining high precision in this type of aerosol work.

A comparison of the results obtained with dry and with oiled chamber walls shows no marked differences (Table III and Fig. 7). It is concluded that particles once deposited were not removed from the dry walls to any serious extent.

Application of Equation (7) to the data for still air yields a value of 2.2×10^{-8} cc. per min. for the constant k (Table III). The coagulation constant for an ideal aerosol as calculated from Equation (13) is 1.9×10^{-8} cc. per min. for particles of 1 μ radius and 2.1×10^{-8} cc. per min. for particles of 0.5 μ radius (cf. Fig. 3). As previously stated the value of K of Equation (1) obtained from the early portion of $1/n$ vs. time plots was 5.1×10^{-8} cc. per min., in agreement with the results of previous workers.

For a homogeneous aerosol the ratio α/β should be unity (Equation 10). For a non-homogeneous aerosol, loss of the heavier particles must be favoured—in sedimentation when the air is still, and in the deflection of air currents at surfaces when the air is in motion. Hence α/β should be greater than unity, but perhaps not very much so if the particle size range is small. Furthermore, both α and β should increase with the rate at which air is brought into contact with surfaces, and if the particle size distribution is not much altered (cf. Fig. 3), they should do so in roughly the same proportion. Both these features are characteristic of the data. It is shown in Fig. 6 that β is quite closely proportional to α regardless of the degree of air motion. It

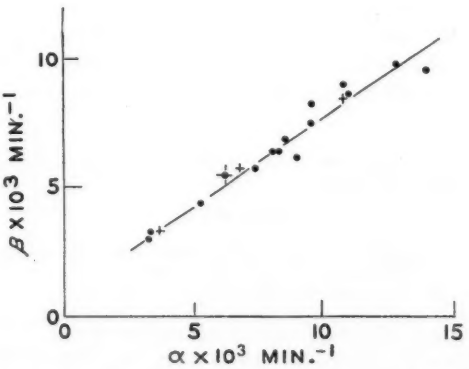

FIG. 6. *To illustrate the interdependence of α and β. The plot includes data for V values from 0 to 50 m. per min. The symbols + denote results obtained with oiled chamber walls.*

is shown in Table III that the ratio α/β is somewhat greater than unity. These facts provide strong support for the ideas advanced in Section 3, since β was determined analytically from particle number data and α directly from

an entirely independent set of mass concentration data. The manner in which α, β, and k increase with the degree of air motion (index, V, m. per min.) is shown in Fig. 7.

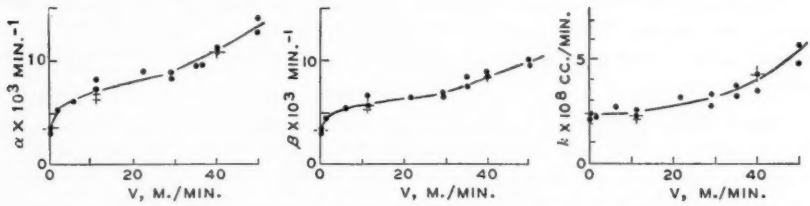

FIG. 7. *Changes in α, β, and k with increasing air motion. The symbols + denote results obtained with oiled chamber walls.*

In view of the wide range of conditions investigated, a purely fortuitous agreement between the equations and the data appears highly unlikely. The equations resulting from integration must be regarded, however, as descriptive of a special case, i.e., that for which time variations in α, β, and k may be disregarded. They would not be expected to apply, for example, to aerosols having a much smaller particle size.

It follows from the ideas expressed in Section 3 that the relative importance of coagulation and surface loss in the ageing process depends strongly on conditions. The importance of the former mechanism should be relatively great for dense aerosols since the rate of coagulation depends on n^2 while the rate of loss depends on n*. During the life of an aerosol the relative importance continually shifts to favour the latter mechanism. For the conditions of the experiments described, the rates of disappearance and the total numbers removed by each mechanism may be calculated separately for any given time with the aid of Equations (4), (5), (8), and (9) and the constants given in Table III.

* *In general, previous investigators have worked with aerosols having an initial particle number several times that of our smokes.*

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AN ACETYL DERIVATIVE OF HEPARIN[1]

By H. J. Bell[2] and L. B. Jaques[3]

Abstract

An acetyl derivative of heparin corresponding to one mole of acetyl per four hexose units has been prepared by passing ketene through a suspension of heparin in acetone. The derivative possesses the same biological activity as the original heparin. It can be deacetylated in neutral solutions without loss of activity by raised temperatures, and like heparin, it is inactivated in acid solution.

Heparin is a polysaccharide possessing a very specific and very marked biological property, namely, its anticoagulant action on blood. Its clinical use has been hindered by the extreme rapidity with which it is excreted or destroyed by the body (Jaques (4)). We therefore thought it of interest to attempt to synthesize derivatives of this substance. However, while heparin is resistant to high temperatures at neutrality, it is very sensitive to acid and alkali (Charles and Scott (1)). Even brief exposure to relatively weak acid or alkali will completely destroy its anticoagulant activity. Hence the usual methods for preparing derivatives of carbohydrates are not suitable for the preparation of heparin derivatives. Hurd, Cantor, and Roe (3) have prepared acetyl derivatives of sugars by passing ketene through a suspension of the sugar in anhydrous acetone. We have applied this method to heparin and succeeded in preparing an acetyl derivative of heparin without any loss in anticoagulant potency.

Methods and Results

Acetyl determinations were made in the Kuhn–Roth apparatus, as described by Roth (9). The sample was hydrolysed by heating at 100° C. for 2½ hr. with 5% aqueous sodium hydroxide. After distillation, the acetic acid was titrated with 0.01 *N* sodium hydroxide. The blank on the reagents was 0.477 ml. of 0.01 *N* sodium hydroxide. The determination of acetyl in acetanilide gave 31.7% acetyl (theoretical, 31.8%).

Anticoagulant activity was determined by means of the Charles and Scott (5) modification of the Howell cat assay. In some cases the product was also checked by Miss A. G. Macdonald for its action on dog's blood *in vitro* and *in vivo*, as described by Jaques and Macdonald (6). The *heparin* used was the neutral sodium salt kindly supplied by the Connaught Medical Research

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Laboratories, University of Toronto, and had an assay value of 110 anti-coagulant units per mgm. It contained 12.1% water, which was removed by drying over phosphorus pentoxide *in vacuo*. pH values were determined with the Beckman glass electrode.

Acetyl Content of Heparin

Since heparin contains glucosamine, Jorpes (7) assumed that it must contain acetyl. However, Charles and Todd (2) reported that they could not get consistent values for the acetyl content of heparin. Masamune, Suzuki, and Kondoh (8) explained this on the basis of a formation of acetic acid from glycuronic acid by sulphuric acid (10%) during the determination. More recently Wolfrom, Weisblat, Karabinos, McNeely, and McLean (10) have reinvestigated this question and failed to find any acetyl in purified heparin.

Determinations of acetyl were conducted on the sample of neutral sodium salt of heparin. These consistently gave a value of 1.13 to 1.20% acetyl, corresponding to an acetyl content of 0.37 mole. However, when the neutral sodium salt of heparin was dissolved in water (pH 6.94), the solution boiled for seven seconds, and then titrated, a titration value equivalent to 0.57% acetyl was obtained. Likewise, this amount of acid could be distilled from the aqueous neutral solution of sodium heparin. It is evident, therefore, that this value is not O- or N- acetyl. This fact was further demonstrated in control experiments on the acetylation procedure.

The neutral sodium salt of heparin was suspended in acetone at 55° C. for three hours. The 'acetyl' content remained at 1.13%. In a second control experiment, a large excess of heparin (0.66 gm.) was suspended in acetone and ketene was passed through for two hours. It had previously been found that no acetylation took place if an excess of heparin was present. The product now contained only 0.64% acetyl (0.2 mole). The latter value was therefore considered to be the 'acetyl' value of heparin itself.

Conducting the hydrolysis with *p*-toluenesulphonic acid instead of sodium hydroxide made no difference in the acetyl value.

As shown by Charles and Todd, the fundamental unit of heparin is a four-hexose unit containing two glucosamine, two glycuronic acid, and five sulphuric acid residues. As the degree of polymerization of this unit and the chain length are both unknown, we have reported our values in moles per four-hexose unit. An increase in the acetyl content of 3.19% is equivalent to the introduction of one mole of acetyl per four-hexose unit.

Preparation of the Acetyl Derivative

The heparin was dried to constant weight *in vacuo* over phosphorus pentoxide at room temperature, and an 88 mgm. sample was suspended in 25 ml. of acetone (freshly distilled from calcium chloride) in a 100 ml. flask. The flask, equipped with a reflux condenser, was placed in a water-bath at approxi-

mately 55° C. and ketene was passed in from a generator for one hour or more. The suspension was then centrifuged, the precipitate washed twice with 5 ml. of acetone, and dried *in vacuo* to give 90.6 mgm. of acetyl heparin. The average acetyl content of the compound was 4.02% and the anticoagulant potency 131 units per mgm.

When ketene was passed through samples for one, two, three, and eight hours, the acetyl content of the samples was 3.98, 4.06, 4.01, and 4.44%, and the biological activity was 130, 130, 131, and 132 units per mgm.

One sample treated with ketene for two hours when freshly prepared gave an acetyl content of 4.61% and a biological activity of 188 units per mgm. It decreased rapidly to 138 units per mgm. in four weeks' time. The sample showing an acetyl content of 4.44% also showed a more intense biological activity when first tested.

Hurd, Cantor, and Roe (3) found that traces of sulphuric acid acted as a catalyst for the acetylation of simple sugars by this method. However, we found that the presence of sulphuric acid may cause inactivation of the heparin. At pH 3.0, 10% of the biological activity was lost; at pH 1.3, a compound was obtained having 4.06% acetyl but only 4% of the biological activity. The sulphuric acid was therefore omitted in the preparation.

Properties of the Acetyl Derivative of Heparin

The compound was stored for a month *in vacuo* over calcium chloride without change in acetyl or biological activity. The effect of temperature on neutral solutions of the compound is shown in Table I. Heating a neutral solution at 70° C. for 30 min. caused no loss in potency of either heparin or

TABLE I

EFFECT OF TEMPERATURE ON NEUTRAL SOLUTION OF HEPARIN AND ACETYL HEPARIN

Substance	Treatment	Biological potency/mgm.	Acetyl, %
Heparin	—	124	0.57
Acetyl heparin	—	131	4.02
Heparin, 3 mgm./ml.	70° C. for one-half hour	130	—
Acetyl heparin, 3 mgm./ml.	70° C. for one-half hour	122	1.58
Heparin, 4 mgm./ml.	Autoclave for one hour[1]	134	—
Acetyl heparin, 4 mgm./ml.	Autoclave for one hour[1]	109	1.31

[1]*15 lb./sq. in.*

the acetyl compound. However, the acetyl compound lost more than half its acetyl by this treatment. Autoclaving for one hour at 15 lb. pressure caused no decrease in anticoagulant potency of heparin itself. There was a slight decrease in the value for the acetyl heparin, and a marked loss in the acetyl content. The effect of pH on the biological activity of heparin is

shown in Table II. Samples (30 mgm.) of heparin and of acetyl heparin were placed in 25 ml. flasks, 10 ml. of water acidified with hydrochloric acid was added to each, and the flasks placed in a water-bath at 50° C. for two hours. The contents of the flasks were then taken to dryness over calcium chloride *in vacuo* and assayed. Both heparin and acetyl heparin rapidly lose their biological activity in acid solution. As apparent, the acetyl compound is the less stable below pH 2.0.

TABLE II

EFFECT OF pH ON THE BIOLOGICAL ACTIVITY OF HEPARIN AND ON ITS ACETYL DERIVATIVE

pH	Biological activity in units/mgm.	
	Heparin, 3 mgm./ml.	Acetyl derivative of heparin, 3 mgm./ml.
1.04	18.7	3.7
1.39	36.9	5.3
2.01	67.2	69.5
3.04	84.4	109.4
3.99	107.2	117.7

Note.—Temperature, 50° C. Time, two hours.

Miss A. G. Macdonald kindly tested a sample of acetyl heparin for its effect on the clotting time of two dogs when injected intravenously as described by Jaques and Macdonald (6). No difference in response was obtained for the acetyl heparin as compared with the original heparin.

Investigations have not been made of the site of attachment of the substituted acetyl. The instability of the linkage makes it doubtful that the acetyl is joined to nitrogen as in glucosamine. Further, it is evident from the results of Charles and Scott, and of Wolfrom, Weisblat, Karabinos, McNeely, and McLean, that in heparin the amino group of glucosamine is substituted, although the substitution does not form as strong a bond as that of acetyl in glucosamine. Formation of acid anhydrides with the neutral sodium salt of heparin appears unlikely. This leaves only the hydroxyl groups of the sugars for substitution. When all the sulphuric acid residues and oxygen bridges in the four-hexose unit are allowed for, five to seven hydroxyl groups remain (10). It is presumed that substitution occurs at these carbons. It would be of interest to study this point in more detail. Whether heparin as it occurs naturally is acetylated, is not known. Certainly, in view of the lability of the acetyl group, it would be lost during the usual procedures of isolating heparin from tissue.

Acknowledgment

We wish to take this opportunity to express our appreciation of the interest and support of Prof. C. H. Best.

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COMPOUND FORMATION IN THE SYSTEM UROTROPINE – ACETIC ACID

I. THE PHASE DIAGRAM[1]

By K. K. Carroll[2] and R. H. Wright[3]

Abstract

The freezing point diagram has been plotted for mixtures of acetic acid and urotropine containing 0 to 42% urotropine. Formation of a solid compound melting at 24.8° C., and having the approximate composition $(C_6H_{12}N_4)_3 \cdot (C_2H_4O_2)_{13}$ is indicated. Repeated purification of the materials failed to shift the curve maximum to the expected ratio of 1 mole of urotropine to 4 moles of acetic acid.

Materials and Experimental Procedure

The urotropine was a commercial preparation supplied by Dr. C. A. Winkler of McGill University. It was twice crystallized from 95% ethanol and dried in a desiccator over concentrated sulphuric acid.

C.p. glacial acetic acid was distilled from potassium dichromate, and the distillate fractionally frozen until the residue froze at or above 16.5° C.

In the determination of the cooling curves, the solutions of urotropine in acetic acid were placed in a double-walled Pyrex tube fitted with a thermometer and ring-shaped glass stirrer. The approximate freezing point was first determined, then the cooling bath was adjusted to 4° to 5° C. lower for the actual measurement of the cooling curve. The freezing point diagram was constructed from the observed breaks and arrests in the cooling curves.

Results and Discussion

A summary of the results is given in Table I, and the freezing point diagram is shown in Fig. 1.

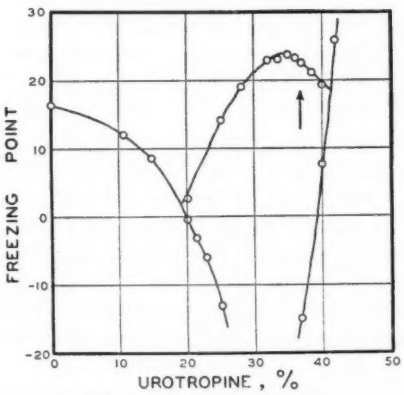

Fig. 1. *Freezing point diagram.*

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The diagram shows the formation of a solid compound with a congruent melting point. Its composition, as indicated by the maximum in the curve, is approximately $(C_6H_{12}N_4)_3 \cdot (C_2H_4O_2)_{13}$. The maximum is fairly sharp; this indicates that there is some association in the liquid state as well.

TABLE I

Urotropine, %	Freezing point, ° C.	Solid phase
0	16.5	Acetic acid
10.7	12.0	" "
14.8	8.5	" "
—	2.4	Eutectic
20.0	−0.4	Acetic acid
20.0	2.6	Compound
21.4	−3.0	Acetic acid
22.8	−6.0	" "
25.0	−13.0	" "
25.0	14.2	Compound
28.0	19.2	"
32.0	23.0	"
33.5	23.1	"
35.0	23.8	"
36.0	23.3	"
36.85	22.8	"
36.85	−15.0	Urotropine
38.5	21.2	Compound
40.0	19.4	"
40.0	7.7	Urotropine
—	18.9	Eutectic
42.0	26.0	Urotropine
(The following measurements were made with anhydrous calcium sulphate added.)		
35.0	24.1	Compound
36.0	23.5	"
36.85	23.2	"
(The following measurements were made with acetic acid, m.p. 14.7° C. containing 0.9% added water.)		
32.0	20.0	Compound
33.5	20.5	"
35.0	20.3	"
36.0	20.1	"

The system shows a marked tendency to supercool and the compound does not crystallize unless the solution is seeded. No solid separated from a 32.5% mixture after two hours at −17° C. A solid did separate, however, when such a mixture was left in the cooling bath overnight. Because of this supercooling, it was possible to follow the freezing point diagram below the eutectic points.

The solid separating from solutions high in urotropine appeared to be urotropine rather than another acetate. It separated more readily when the solution was seeded with urotropine, and the crystals when filtered and dried with filter paper decomposed from 210° to 260° C. in a melting point tube. More than 42% urotropine could not be dissolved in acetic acid, and heating to higher temperatures caused decomposition.

The presence of four nitrogen atoms in urotropine makes the formation of a tetra-acetate seem logical, and the maximum in the curve is near the required composition. At the same time, it does not coincide exactly with the required composition: the arrow in Fig. 1 shows the composition corresponding to urotropine tetra-acetate. This anomaly was investigated in some detail.

Thus, as a further purification, the acetic acid was frozen out repeatedly until it melted at 16.7° C.; further fractional freezing did not raise the melting point. A solution made from this acid and containing 36.85% urotropine had a freezing point of 23.0° C., which was lower than that of a 35.0% solution made with acetic acid of melting point 16.5° C.

Again, the purified urotropine was analysed for formaldehyde and ammonia by the method of Carmack (1). Found: formaldehyde, 127.6%; ammonia, 48.59%. Calc.: formaldehyde, 128.5%; ammonia, 48.60%.

This agreement is reasonably good and indicates that there is no significant amount of impurity in the urotropine. Also, when the urotropine was further purified by sublimation *in vacuo* at 160° to 180° C., the freezing points of solutions containing 35.0 and 36.85% urotropine respectively were unchanged. The same results were obtained when the urotropine was purified by crystallization from absolute methanol. It seems unlikely from these results that the discrepancy was caused by impurity in the urotropine.

The effect of water as a third component was shown by a series of solutions containing 0.9% added water. This displaced the curve downward about 3° C. and flattened it somewhat, and the peak was shifted to approximately 33.5% urotropine. Thus it was thought that an absolutely anhydrous medium might show a maximum at 36.85% urotropine. Anhydrous calcium sulphate was added to a normal series of solutions in an effort to remove traces of water without interfering with the freezing points. In such a series, the freezing points were all slightly higher than they were before, but there was no perceptible shift in the peak towards 36.85% urotropine.

In a further attempt to show the composition of the compound, crude urotropine was dissolved in reagent acetic acid (1 mole in 4) to give about 400 gm. of solution. This was seeded with the compound and allowed to freeze slowly so that large crystals formed. The mixture was kept in a stoppered separatory funnel and the unfrozen liquid drained off. The crystals were then melted and allowed to freeze again slowly and the residual liquid again removed. This process was repeated 10 times. The final crystals melted at 24.8° C. They were analysed for formaldehyde and ammonia contents and the results expressed as the percentage of urotropine. Found: formaldehyde, 33.83%; ammonia, 34.52%.

It was further found that the presence of urotropine does not interfere in the titration of acetic acid with sodium hydroxide using phenolphthalein. Titration of a sample of the above crystals melting at 24.8° C. gave 65.52% acetic acid corresponding to 34.48% urotropine. This is in good agreement with the formaldehyde and ammonia analyses.

In all the experiments, higher melting points were obtained with solutions containing 34 to 35% urotropine rather than those containing 36.85%, which corresponds to the more plausible tetra-acetate formula. An impurity would be expected to lower the whole curve and could also displace the maximum. However, no direct evidence for such an impurity was obtained and its presence remains purely hypothetical.

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COMPOUND FORMATION IN THE SYSTEM UROTROPINE – ACETIC ACID

II. RAMAN SPECTRUM MEASUREMENTS[1]

By K. K. Carroll[2] and R. H. Wright[3]

Abstract

The Raman spectrum of a solution of urotropine in acetic acid (1 mole in 4) has been measured. The results are interpreted as indicating partial combination of the two in the liquid state. The presence of ammonium nitrate in amounts up to 1% caused no observable change in the Raman spectrum. Increasing the temperature of the solution containing ammonium nitrate to 50° to 60° C. resulted only in a uniform darkening of the lines.

It has previously been shown (1) that urotropine and acetic acid form a solid compound melting at 24.8° C. The present work was designed to reveal the existence of combination in the liquid state. Information was also desired on the effect of small amounts of ammonium nitrate.

Materials, Apparatus, and Experimental Procedure

The materials were purified as in the previous work (1).

A Bausch and Lomb constant deviation glass spectrograph (f 17.2) was used in photographing the Raman spectra.

The source was a coiled mercury discharge lamp (30 coils) which surrounded a Raman tube consisting of two concentric glass tubes, the outer one serving as a jacket for holding filters.

The 4358 mercury line was used as the exciting radiation. Two filters were used for isolating this line. The 4046 mercury line was absorbed by filling the outer jacket of the Raman tube with a 25% solution of nitrobenzene in ethanol (2 mm. layer). The 4916 mercury line and the continuous background between it and 4358 were reduced by a gelatin filter stained with crystal violet. This was prepared by dipping the Raman tube in a 12% solution of gelatin at 50° to 60° C., allowing it to dry, and then dipping it in a 0.6% solution of crystal violet in water, and again allowing it to dry.

The exposures were of 90 hr. duration. The mercury lamp generated enough heat to maintain the Raman tube at 50° to 60° C. unless it was kept at room temperature by means of an electric fan. (This was done except where otherwise stated.)

The comparison spectrum consisted of the superimposed lines of mercury, helium, and argon discharge tubes.

[1] *Manuscript received November 6, 1946.*

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, N.B. This work was carried out with the assistance of a grant from the National Research Council.

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[3] *Present address: Head, Division of Chemistry, British Columbia Research Council.*

The frequency separation of the Raman lines was measured by a projection apparatus as suggested by Hibben (2). The apparatus was calibrated by measuring the linear separation of the lines in the comparison spectrum and plotting against the known separation in wave numbers. The wave number separation of the Raman lines was read directly from this graph after the linear separation had been measured. The relative intensities of the lines were judged visually on a 0 to 10 scale.

All photographs were taken on Eastman spectrographic plates (Type 103-F). Development was for five minutes at 20° C. using Eastman formula D-19 developer, and the plates were fixed for 15 min. with Eastman F-5 acid-hardening, fixing solution.

Results and Discussion

The Raman spectra of acetic acid and of urotropine, both crystalline and in aqueous solution, have been measured by a number of investigators (3). The spectrum of acetic acid was repeated to give an estimate of the light-gathering power of the spectrograph and to check the method of calibration. With the apparatus available, it was not possible to observe the Raman spectrum of the urotropine – acetic acid compound in the solid state.

A solution of urotropine in acetic acid (mole ratio 1:4) was photographed with and without the addition of 0.32% of ammonium nitrate. No difference was observed in the two spectra. By raising the temperature to 50° to 60° C., 1.08% of ammonium nitrate could be kept in solution, but again no difference was observed apart from a general darkening of the lines.

The photographs of the Raman spectra of acetic acid and of the urotropine – acetic acid solution are reproduced in Fig. 1. The Raman shifts and relative intensities of the lines are given in Table I. Fig. 2 gives a graphical comparison of these results with those of other workers.

TABLE I

EXPERIMENTAL RESULTS

The numbers give the separations of the Raman lines from the exciting line, expressed in wave numbers. The figures in parentheses indicate the relative intensities. *b* = broad; *sb* = medium broad; *d* = diffuse.

Acetic acid:	450 ($\frac{1}{2}$); 624 (2); 899 (5); 1354 ($\frac{1}{2}b$); 1436 (2*b*); 1670 (2*b*); 2945 (10); 2986 ($\frac{1}{2}$); 3028 ($\frac{1}{2}$).
Urotropine + acetic acid (1:4 moles):	457 (2); 507 (1); 616 ($\frac{1}{2}$); 703 (0?); 792 (3*b*); 891 (4*sb*); 941 (0); 1025 (1); 1071 (0?); 1356 (4); 1451 (4*b*); 1721 (1*d*); 2940 (10*b*); 3003 (6*b*).

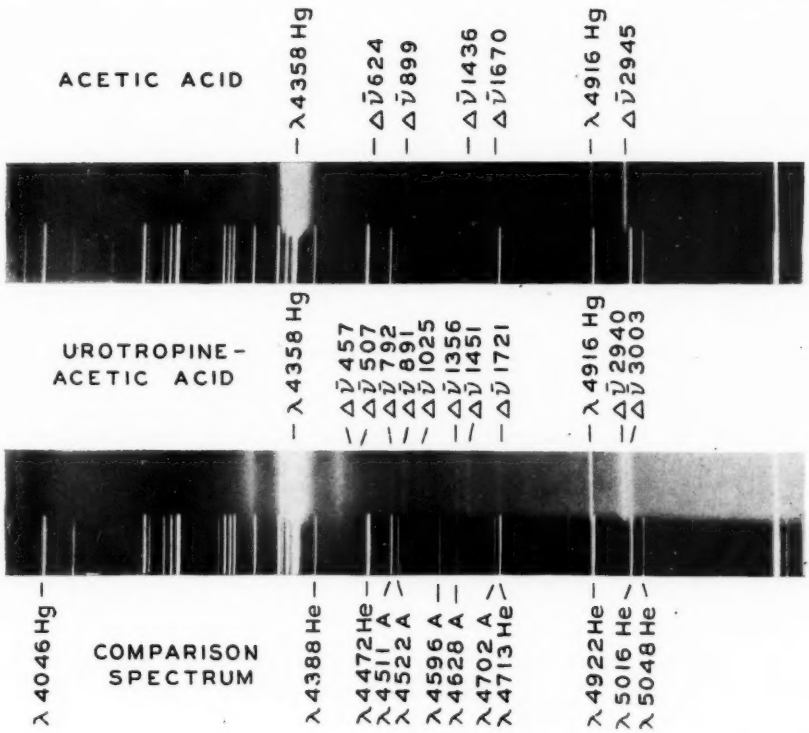
ACETIC ACID
λ 4358 Hg
Δν̄ 624
Δν̄ 899
Δν̄ 1436
Δν̄ 1670
λ 4916 Hg
Δν̄ 2945
UROTROPINE-
ACETIC ACID
λ 4358 Hg
Δν̄ 457
Δν̄ 507
Δν̄ 792
Δν̄ 891
Δν̄ 1025
Δν̄ 1356
Δν̄ 1451
Δν̄ 1721
λ 4916 Hg
Δν̄ 2940
Δν̄ 3003
λ 4046 Hg
COMPARISON
SPECTRUM
λ 4388 He
λ 4472 He
λ 4511 A
λ 4522 A
λ 4596 A
λ 4628 A
λ 4702 A
λ 4713 He
λ 4922 He
λ 5016 He
λ 5048 He

FIG. 1

The results show that nearly all the lines obtained in the urotropine – acetic acid solution correspond with lines of either acetic acid or urotropine. There are two notable exceptions.

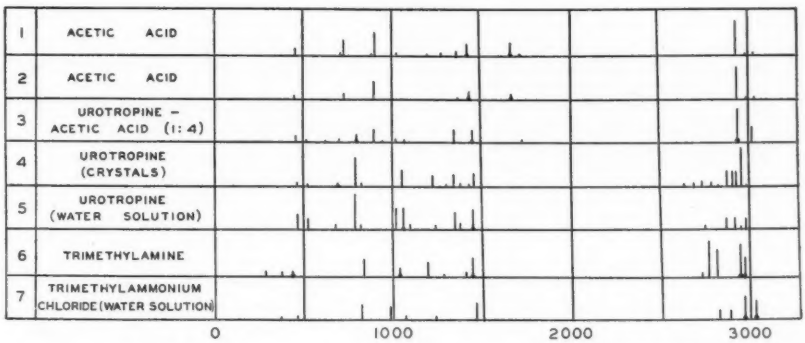

FIG. 2. *The values in 2 and 3 are from the present work. The remainder are taken from Kohlrausch (3).*

The line $\Delta\bar{\nu}$ 1666-1670 of acetic acid is not present in the solution but is replaced by a fainter and more diffuse line at $\Delta\bar{\nu}$ 1721. A similar change has been observed when acetic acid is diluted with a number of solvents (2). The line at $\Delta\bar{\nu}$ 1666 is generally ascribed to the $-C=O$ group in the dimeric molecules of acetic acid, and the $\Delta\bar{\nu}$ 1700 line to the monomeric form (2). The presence of either of these lines is evidence that the liquid contains some free acetic acid. In acetates, such as sodium and ammonium acetate, these frequencies disappear and a strong line is found in the vicinity of $\Delta\bar{\nu}$ 1400 (3). Urotropine itself has several strong lines in the vicinity of $\Delta\bar{\nu}$ 1400, so that it was not possible to detect this line in the present case.

The second important change in the spectrum is the disappearance of several urotropine lines near $\Delta\bar{\nu}$ 2900 and the appearance of a single heavy and rather broad line at $\Delta\bar{\nu}$ 3003. This line may be due to an N-H vibration in a urotropine acetate. Lines due to N-H vibrations usually occur in the range $\Delta\bar{\nu}$ 3200-3400, but smaller separations are usual in ammonium and substituted ammonium salts (3). For example, dimethyl- and trimethylamine hydrochlorides give lines at $\Delta\bar{\nu}$ 3040 and the propylammonium ion gives a line at $\Delta\bar{\nu}$ 2980. The Raman spectra of trimethylamine and trimethylamine hydrochloride are given for comparison in Fig. 2. Urotropine hydrochloride has been studied in the crystal form by Krishnamurti (4), who gives the values 444 (1), 713 (3), and 856 (1) with no long frequencies. It is possible that lines of large frequency separation were present but were not observed.

Several other changes are observable in the new spectrum, such as the disappearance of a urotropine line at $\Delta\bar{\nu}$ 1234, but since such lines have not been associated with any particular vibration in the molecule, it is difficult to interpret these changes.

In general, the results support the conclusion that urotropine combines with acetic acid in the liquid state as well as in the solid state.

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QUANTITATIVE ESTIMATION AS ACETIC ACID OF ACETYL, ETHYLIDENE, ETHOXY, AND α-HYDROXYETHYL GROUPS[1]

By R. U. Lemieux[2] and C. B. Purves[3]

Abstract

Kuhn and L'Orsa's method for estimating terminal methyl and similar groups was based on the recovery of the acetic acid formed when such units were oxidized with hot concentrated chromic acid solution. The method has now been reduced to the semimicro scale and refined to the point where good analyses for acetyl, ethylidene, ethoxy, and α-hydroxyethyl groups in a variety of substances are obtained. Acetylated triphenylmethyl cellulose ethers, which do not seem amenable to customary acetyl analyses, give good results by the present procedure.

Introduction

During an extension of published work on the acetylation of cellulose trityl (triphenylmethyl) ether (5, 11, 12), standard methods of acetyl analysis proved to yield low results. Those tried were the sodium methylate saponification – *p*-toluenesulphonic acid – methanol distillation method of Cramer, Gardner, and Purves (1), the modification of the Ost distillation technique by Genung and Mallatt (2), and saponification in a homogeneous medium as described by Malm, Genung, Williams, and Pile (9). Although all three methods gave concordant and correct results in the absence of the trityl ether unit, in its presence each, although often fairly reproducible in duplicate estimations, was low by a variable amount. Attempts made on samples containing added triphenylmethyl carbinol to determine the cause of these aberrations led to no definite conclusion. In these circumstances attention was given to the oxidations of organic substances by Kuhn and L'Orsa (7), who employed a hot concentrated aqueous solution of chromium trioxide. These authors found that in many cases a steam distillation of the oxidizing mixture recovered acetyl, ethoxy, and terminal methyl groups as acetic acid, the yield of acetic acid often being more than 85% of theory. Their results were confirmed, for terminal methyl groups in the lignin series, by MacGregor, Evans, and Hibbert (8). The present article describes a semimicro adaptation of the estimation, which gave practically quantitative results. Although in blank runs the acidity of the distillate varied from 0.5 to 1.3 ml. of 0.02 *N* alkali with slight variations in operating conditions, for a given apparatus and given reagents this blank was in a fixed ratio to the oxidizing equivalent of the distillate in terms of 0.02 *N* sodium thiosulphate solution. Ratios of 1.33 to 1, and 0.91 to 1, for example, were observed with two sets of equipment used at different times. This blank acidity was presumably caused by

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volatile impurities in the reagents and by the entrapment of traces of chromic acid in the distillate. Knowledge of the factor relating number of cubic centimetres of alkali to number of cubic centimetres of thiosulphate in the blanks made it possible to dispense with separate blank determinations in routine estimations with the same equipment and reagents.

Description of the Method

Reagents

1. Aqueous 30% chromium trioxide,
2. Carbon dioxide-free 0.020 *N* sodium hydroxide,
3. Standard 0.020 *N* sodium thiosulphate,
4. Iodate-free potassium iodide,
5. Aqueous 10% sulphuric acid,
6. Sodium bicarbonate,
7. Indicator solutions: phenolphthalein, 1% amylose.

Procedure

A 15 to 50 mgm. sample (depending on the amount of acetic acid produced) was weighed into a 100 ml. round-bottomed flask equipped with a ground glass joint (Fig. 1). The sample was covered with 10 ml. of the 30% chromic

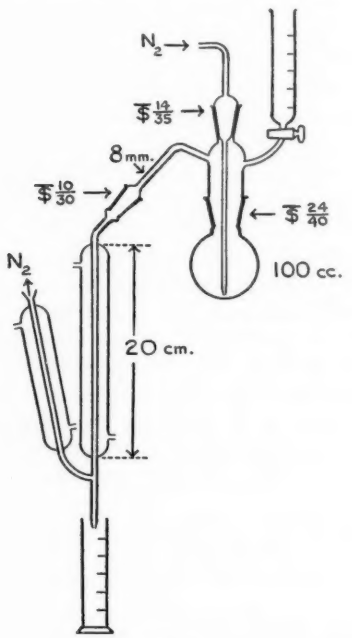


FIG. 1.

acid solution, the flask was two-thirds immersed in an oil-bath, the apparatus (Fig. 1) was assembled, and nitrogen gas was passed through it at a rate of one to two bubbles per second. The temperature of the bath was then raised to 155° C. within one-half hour by means of a hot-plate and was maintained at this figure until the end of the determination. Too rapid an initial rise in temperature resulted in high blanks. Distillation began at 135° to 140° C. and, as successive 5 ml. volumes of distillate collected in the 50 ml. graduate, 5 ml. volumes of distilled water were added to the still from the 50 ml. graduated dropping funnel. This procedure was continued until 50 ml. of water had been added and 55 ml. of a very faintly yellow distillate had been collected. The condenser was then detached from the still-head and both arms of the former were washed with distilled water, the washings being collected in a 250 ml. Erlenmeyer flask. The contents of the graduate was then quantitatively transferred to the same flask and the combined solution was titrated with standard carbon dioxide-free 0.020 *N* sodium hydroxide solution until the end-point just began to fade (phenolphthalein indicator). The liquor was then brought to a boil to remove carbon dioxide, cooled to room temperature under the cold water tap, and the titration continued until the pink coloration remained stable for 10 sec. Note was taken of the volume, x, of standard alkali used. Approximately 0.5 gm. of sodium bicarbonate was then added, followed by 10 ml. of 10% sulphuric acid, and, after carbon dioxide evolution had ceased, by 1 gm. of potassium iodide. The flask was stoppered, shaken, and kept in the dark for five minutes, after which time the liberated iodine was titrated with 0.020 *N* sodium thiosulphate. This titration, y cc., when multiplied by the empirical factor K appropriate to the particular apparatus and reagents in use, gave the acid equivalent *not* caused by acetic acid. The acetic acid equivalent was therefore $(x - Ky)$ cc. of 0.02 *N* alkali.

Two and one-half hours was required for the estimation.

Table I shows that the oxidation quantitatively recovered the terminal methyl groups in the first two compounds as acetic acid and is therefore valid for primary desoxy groups in carbohydrates. Since the chromic acid oxidation does not demand the presence of an unsubstituted 1,2-glycol unit adjacent to the methyl group, it is certainly more widely applicable than the periodate-oxidation technique developed by Nicolet and Shinn (10), and is probably just as convenient. Determinations of the ethylidene group in a sample of monoethylidene methyl-α-glucopyranoside prepared by Hill and Hibbert (6), and of the ethoxy groups in a technical ethylcellulose, were also successful. The method should find application for group analyses in ethylidene derivatives of polyhydroxy substances and for the estimation of ethoxy in presence of methoxy groups. Analyses for acetyl content in the absence of trityl units agreed well both with theory and with the results of other standard methods. The present procedure also gave a satisfactory result with 6-trityl methyl-α-glucopyranoside triacetate.

TABLE I

ACETYL AND TERMINAL METHYL GROUP ESTIMATIONS

Compound	Sample, mgm.	Correction blank, *K*y ml.[1]	'Total acetyl'	
			% Calc.	% Found
Rhamnose hydrate	37.5	0.45	23.6	23.2
Isorhamnose tetraacetate	19.9	0.80	64.8	64.5
Monoethylidene methyl-α-glucoside	52.4	0.36	19.6	19.5
Ethylcellulose[2]	50.4	0.48	26.4	26.3
Glucose pentaacetate	24.8	0.80	55.0	55.0
Methyl-α-glucoside tetraacetate	21.3	0.77	47.5	47.5
Cellulose acetate[3]	29.1	0.60	38.6	38.8
6-Trityl methyl-α-glucoside triacetate[4]	49.3	0.82	23.0	23.6
	54.1	0.55	23.0	23.4
Trityl cellulose acetate[5]	70.3	1.33	17.4[5]	17.5
	55.4	0.81	—	17.2

[1] *Ml. of 0.02 N caustic soda.*

[2] *Presented by the Hercules Powder Co. Sample X 2167-12; of 27.6% ethoxy content by standard alkoxyl estimation.*

[3] *Presented by the Eastman Kodak Co. An acetone soluble grade with 38.6% acetyl.*

[4] *Old sample of Gladding and Purves (3). M.p. 145° to 147° C. (uncorr.) instead of m.p. 142° to 145° C. (corr.).*

[5] *See Table II.*

TABLE II

ACETYL CONTENT OF TRITYL CELLULOSE ACETATES

Trityl cellulose	Acetylated products[1]				Other acetyl analyses
	% Trityl[2]	% Acetyl	Moles trityl[3]	Moles acetyl[3]	
I	50.5	15.3	0.98	1.67	10.7[4]
XI	51.7	13.9	0.99	1.49	9.3, 12.2[5]
XI	51.7	14.5	1.00	1.55	—
XI	49.5	18.0	0.99	2.01	—
XI	50.2	17.4[8]	1.02	1.98	14.0, 14.6[6]
—[7]	52.3	13.8	1.01	1.51	9.6, 9.2[4]

[1] *With acetic anhydride, or acetyl chloride, in pyridine for various times at various temperatures.*

[2] *Analyzed by Hearon, Hiatt, and Fordyce method (4).*

[3] *For calculation see text.*

[4] *Cramer, Gardner, and Purves method (1).*

[5] *Method of Malm, Genung, Williams, and Pile (9).*

[6] *Genung and Mallatt method (2).*

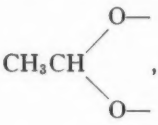
[7] *Prepared by Dr. V. R. Grassie.*

[8] *See Table I.*

Table II summarizes the analyses of a series of acetates derived from three different preparations of cellulose monotrityl ether. The molar substitutions per glucose unit of trityl and acetyl were readily calculated from the percentage figures by means of a simultaneous equation. Since acetylation for various times in pyridine solution was not likely to affect the trityl unit, the fact that

the trityl substitution remained close to the correct value of unity while the acetyl content varied is good evidence that the analyses for acetyl, as well as for trityl, are reliable. Other analyses for acetyl, shown to the right of the table, were low.

Consideration of the above results, together with those of the previous investigators (7, 8) shows that the chromic acid oxidation method must be restricted to terminal methyl groups that oxidize quantitatively to acetic acid. This condition is satisfied when the carbon atom adjacent to the methyl group is directly linked to at least one oxygen atom, as in CH_3CH_2—O—,



, CH_3CHOH—, or CH_3COO—. The method fails with compounds such as toluene, cellulose propionates and butyrates, in which the adjacent carbon atom is not substituted by oxygen, because the production of acetic acid from the terminal methyl group is not quantitative. Such compounds constitute interfering substances. Interference was also caused by the allyl ether group, $CH_2=CH—CH_2—O—$, which was found by Dr. L. A. Cox to yield a small amount of volatile acid in the chromic acid oxidation.

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